The geometry of Gibbs-Duhem-Pfaff thermochemical systems

CRISTINA STAMIN
University Politehnica of Bucharest
Faculty of Applied Sciences
Department of Mathematics
Splaiul Independentei 313
060042, BUCHAREST, ROMANIA

CONSTANTIN UDRISTE
University Politehnica of Bucharest
Faculty of Applied Sciences
Department of Mathematics
Splaiul Independentei 313
060042, BUCHAREST, ROMANIA

Abstract: The paper deals with problems concerning simple thermochemical systems dynamics, modelled by Gibbs-Duhem-Pfaff equation. Section 1 analyzes the Gibbs-Duhem-Pfaff equation and the associated nonholonomic hypersurface, consisting in integral manifolds with the dimension at most 3. In Section 2 there are listed 6 simple thermodynamical systems with one state. Section 3 describes 15 simple thermodynamical systems with two states. Section 4 defines 20 simple thermodynamical systems with three states. The simple thermodynamical systems depending on measurable state variables are emphasized.

Key–Words: Nonholonomic hypersurface, integral manifolds, simple thermochemical system, measurable states.

1 Gibbs-Duhem-Pfaff equation and its solutions

The Gibbs-Duhem-Pfaff (GDP for short) equation

$$SdT - VdP + \sum_{i=1}^{n} N_i d\mu_i = 0$$

models the dynamics of thermodynamical behavior of chemical systems made of n types of particles ([1]). There are N_i particles of each type, and the chemical potential of each of them is μ_i. In the previous relation S denotes the entropy, T is the temperature, V is the volume and P denotes the pressure.

In this paper we study chemical systems made of one type of particles. Thus, we consider the 6-dimensional Euclidean space $\mathbf{R}^6$ with the coordinates S, T, V, P, N, μ, and in this space the GDP equation for a substance made of particles of only one type is

$$\omega = SdT - VdP + Nd\mu = 0. \tag{1}$$

We are looking for the solutions (integral manifolds) of GDP equation. For this we need to check the complete integrability condition. Having

$$d\omega = dS \wedge dT - dV \wedge dP + dN \wedge d\mu,$$

and the exterior product

$$\begin{aligned}\omega \wedge d\omega = &-SdT \wedge dV \wedge dP + SdT \wedge dN \wedge d\mu - \\ &-VdP \wedge dS \wedge dT - VdP \wedge dN \wedge d\mu + \\ &+Nd\mu \wedge dS \wedge dT - Nd\mu \wedge dV \wedge dP,\end{aligned}$$

we get that the GDP equation is not completely integrable, because $\omega \wedge d\omega \neq 0$.

To write the matrix attached to the 2-form

$$\theta = d\omega = dS \wedge dT - dV \wedge dP + dN \wedge d\mu,$$

we use the representation $\theta = \sum_{i=1}^{3} dx^i \wedge dy^i$, where

$$\left(x^i\right)_{i=1..3} = (S, V, N), \quad \left(y^i\right)_{i=1..3} = (T, P, \mu).$$

We find the matrix

$$\begin{aligned}[\theta_{d\wedge d}] &= \begin{pmatrix} \theta_{dS\wedge dS} & \theta_{dS\wedge dT} & \cdots & \theta_{dS\wedge d\mu} \\ \theta_{dT\wedge dS} & \theta_{dT\wedge dT} & \cdots & \theta_{dT\wedge d\mu} \\ \cdots & \cdots & \cdots & \cdots \\ \theta_{d\mu\wedge dS} & \theta_{d\mu\wedge dT} & \cdots & \theta_{d\mu\wedge d\mu} \end{pmatrix} \\ &= \begin{pmatrix} 0 & \frac{1}{2} & 0 & 0 & 0 & 0 \\ -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2} \\ 0 & 0 & 0 & 0 & -\frac{1}{2} & 0 \end{pmatrix},\end{aligned}$$

whose determinant is not zero, so the matrix is nondegenerated. These two properties (the analytical condition - the exterior differential of θ is not zero, and the algebraic condition - the nondegenerate matrix) implies that the 2-form θ is a symplectic form on the manifold $R^{2\times 3}$.

Because θ is not degenerated, the 3-form $\theta^3 = \theta \wedge \theta \wedge \theta$ is not zero. The form $\dfrac{\theta^3}{3!}$ is called symplectic volume or Liouville form of the symplectic manifold $(R^{2\times 3},\theta)$. Thus, we have the following

1.1. Proposition. *The integral submanifolds of GDP equation are 1-dimensional, 2-dimensional and 3-dimensional.*

In the sequel these integral submanifolds are described as regular functions of class C^2.

1.2. Definition. *The nonholonomic hypersurface* $(\mathbf{R}^6,\omega=0)$ *is called thermochemical system of GDP type.*

1) An *integral curve* of the GDP equation is a regular function $c : I \subset \mathbf{R} \to \mathbf{R}^6$, $c(t) = (S(t),T(t),V(t),P(t),N(t),\mu(t))$ of C^2 class whose components verify the ODE

$$S\frac{dT}{dt} - V\frac{dP}{dt} + N\frac{d\mu}{dt} = 0. \tag{2}$$

1.3. Definition. *An integral curve of the GDP equation is called thermochemical system with one state.*

If we consider a point $M_0\,(S_0,T_0,V_0,P_0,N_0,\mu_0)$ and a nonzero vector $q=(q_1,q_2,q_3,q_4,q_5,q_6)$ satisfying the condition

$$S_0q_2 - V_0q_4 + N_0q_6 = 0,$$

then there are infinitely many solutions $c(t)$ of the equation (2) satisfying the initial condition $c(t_0) = M_0$.

An integral curve can also be characterized by the algebraic system

$$c_i(S,T,V,P,N,\mu)=0,\ \ i=\overline{1,5},$$

attached to the submersion

$$c=(c_1,c_2,c_3,c_4,c_5):\mathbf{R}^6\to\mathbf{R}^5,$$

having the property that the GDP equation is a consequence of

$$\begin{aligned} c_i(S,T,V,P,N,\mu) &= 0,\\ dc_i(S,T,V,P,N,\mu) &= 0,\ \ i=\overline{1,5}. \end{aligned}$$

2) An *integral surface* of Gibbs-Duhem-Pfaff equation is a regular function $g : D \subset R^2 \to R^6$ of C^2 class whose components $(S(x,y),T(x,y),V(x,y),P(x,y),N(x,y),\mu(x,y))$ verify the PDE system

$$\left\{\begin{array}{l} S\frac{\partial T}{\partial x} - V\frac{\partial P}{\partial x} + N\frac{\partial \mu}{\partial x} = 0\\ S\frac{\partial T}{\partial y} - V\frac{\partial P}{\partial y} + N\frac{\partial \mu}{\partial y} = 0. \end{array}\right. \tag{3}$$

The conditions of complete integrability

$$\frac{\partial^2 T}{\partial x\partial y}=\frac{\partial^2 T}{\partial y\partial x},\frac{\partial^2 P}{\partial x\partial y}=\frac{\partial^2 P}{\partial y\partial x},\frac{\partial^2 \mu}{\partial x\partial y}=\frac{\partial^2 \mu}{\partial y\partial x},$$

get the area condition

$$\begin{array}{c} \frac{\partial T}{\partial x}\frac{\partial S}{\partial y} - \frac{\partial S}{\partial x}\frac{\partial T}{\partial y} + \frac{\partial V}{\partial x}\frac{\partial P}{\partial y} - \\ \frac{\partial P}{\partial x}\frac{\partial V}{\partial y} + \frac{\partial \mu}{\partial x}\frac{\partial N}{\partial y} - \frac{\partial N}{\partial x}\frac{\partial \mu}{\partial y} = 0. \end{array} \tag{4}$$

1.4. Definition. *An integral surface of the GDP equation is called thermochemical system with two states.*

Consider a point $M_0\,(S_0,T_0,V_0,P_0,N_0,\mu_0)$ and two nonzero vectors $q=(q_1,q_2,q_3,q_4,q_5,q_6$ and $r=(r_1,r_2,r_3,r_4,r_5,r_6)$ such that

$$\begin{array}{c} S_0q_2 - V_0q_4 + N_0q_6 = 0,\\ S_0r_2 - V_0r_4 + N_0r_6 = 0,\\ q_2r_1 - q_1r_2 + q_3r_4 - q_4r_3 + q_6r_5 - q_5r_6 = 0. \end{array}$$

There exists an infinity of integral surfaces g satisfying the relations

$$\begin{array}{c} g(x_0,y_0)=M_0,\\ \frac{\partial g}{\partial x}(x_0,y_0)=q,\\ \frac{\partial g}{\partial y}(x_0,y_0)=r. \end{array}$$

An integral surface can be also characterized by the system of equations

$$g_i(S,T,V,P,N,\mu)=0,\ \ i=\overline{1,4},$$

which are attached to the submersion

$$g=g_i(S,T,V,P,N,\mu):\mathbf{R}^6\to\mathbf{R}^4,$$

and which have the property that GDP equation is a consequence of:

$$\begin{aligned} g_i(S,T,V,P,N,\mu) &= 0,\\ dg_i(S,T,V,P,N,\mu) &= 0,\ \ i=\overline{1,4}. \end{aligned}$$

3) An *integral hypersurface of dimension 3* of GDP equation is a C^2 regular function $s : D \subset R^3 \to R^6$ with six components $S(x,y,z)$, $T(x,y,z)$, $V(x,y,z)$, $P(x,y,z)$, $N(x,y,z)$, $\mu(x,y,z)$.

1.5. Definition. *An integral hypersurface of dimension 3 of the GDP equation is called thermochemical system with three states.*

The components of this regular function verifies the PDE system

$$\left\{\begin{array}{l} S\frac{\partial T}{\partial x} - V\frac{\partial P}{\partial x} + N\frac{\partial \mu}{\partial x} = 0\\ S\frac{\partial T}{\partial y} - V\frac{\partial P}{\partial y} + N\frac{\partial \mu}{\partial y} = 0\\ S\frac{\partial T}{\partial z} - V\frac{\partial P}{\partial z} + N\frac{\partial \mu}{\partial z} = 0. \end{array}\right. \tag{5}$$

From the complete integrability conditions

$$\begin{array}{c} \frac{\partial^2 T}{\partial x\partial y}=\frac{\partial^2 T}{\partial y\partial x},\ \frac{\partial^2 T}{\partial x\partial z}=\frac{\partial^2 T}{\partial z\partial x},\ \frac{\partial^2 T}{\partial z\partial y}=\frac{\partial^2 T}{\partial y\partial z},\\ \frac{\partial^2 P}{\partial x\partial y}=\frac{\partial^2 P}{\partial y\partial x},\ \frac{\partial^2 P}{\partial x\partial z}=\frac{\partial^2 P}{\partial z\partial x},\ \frac{\partial^2 P}{\partial z\partial y}=\frac{\partial^2 P}{\partial y\partial z},\\ \frac{\partial^2 \mu}{\partial x\partial y}=\frac{\partial^2 \mu}{\partial y\partial x},\ \frac{\partial^2 \mu}{\partial x\partial z}=\frac{\partial^2 \mu}{\partial z\partial x},\ \frac{\partial^2 \mu}{\partial z\partial y}=\frac{\partial^2 \mu}{\partial y\partial z}, \end{array}$$

one can get the area conditions

$$(6)\quad \begin{cases} \frac{\partial S}{\partial y}\frac{\partial T}{\partial x} - \frac{\partial V}{\partial y}\frac{\partial P}{\partial x} + \frac{\partial N}{\partial y}\frac{\partial \mu}{\partial x} - \\ \frac{\partial S}{\partial x}\frac{\partial T}{\partial y} + \frac{\partial V}{\partial x}\frac{\partial P}{\partial y} - \frac{\partial N}{\partial x}\frac{\partial \mu}{\partial y} = 0 \\ \frac{\partial S}{\partial z}\frac{\partial T}{\partial x} - \frac{\partial V}{\partial z}\frac{\partial P}{\partial x} + \frac{\partial N}{\partial z}\frac{\partial \mu}{\partial x} - \\ \frac{\partial S}{\partial x}\frac{\partial T}{\partial z} + \frac{\partial V}{\partial x}\frac{\partial P}{\partial z} - \frac{\partial N}{\partial x}\frac{\partial \mu}{\partial z} = 0 \\ \frac{\partial S}{\partial z}\frac{\partial T}{\partial y} - \frac{\partial V}{\partial z}\frac{\partial P}{\partial y} + \frac{\partial N}{\partial z}\frac{\partial \mu}{\partial y} - \\ \frac{\partial S}{\partial y}\frac{\partial T}{\partial z} + \frac{\partial V}{\partial y}\frac{\partial P}{\partial z} - \frac{\partial N}{\partial y}\frac{\partial \mu}{\partial z} = 0. \end{cases}$$

For a point $M_0\,(S_0, T_0, V_0, P_0, N_0, \mu_0)$ and three nonzero vectors

$$q = (q_1, q_2, q_3, q_4, q_5, q_6),$$
$$r = (r_1, r_2, r_3, r_4, r_5, r_6),$$
$$p = (p_1, p_2, p_3, p_4, p_5, p_6),$$

complying with

$$S_0 q_2 - V_0 q_4 + N_0 q_6 = 0,$$
$$S_0 r_2 - V_0 r_4 + N_0 r_6 = 0,$$
$$S_0 p_2 - V_0 p_4 + N_0 p_6 = 0,$$
$$q_2 r_1 - q_1 r_2 + q_3 r_4 - q_4 r_3 + q_6 r_5 - q_5 r_6 = 0,$$
$$p_2 r_1 - p_1 r_2 + p_3 r_4 - p_4 r_3 + p_6 r_5 - p_5 r_6 = 0,$$
$$p_2 q_1 - p_1 q_2 + p_3 q_4 - p_4 q_3 + p_6 q_5 - p_5 q_6 = 0,$$

there exists an infinity of integral hypersurfaces s of dimension 3 satisfying the relations

$$s(x_0, y_0, z_0) = M_0, \frac{\partial s}{\partial x}(x_0, y_0, z_0) = q,$$
$$\frac{\partial s}{\partial y}(x_0, y_0, z_0) = r, \frac{\partial s}{\partial z}(x_0, y_0, z_0) = p.$$

We can characterize also an integral hypersurface of dimension 3 by a system

$$s_i(S, T, V, P, N, \mu) = 0, \;\; i = \overline{1, 3},$$

whose equations are attached to the submersion

$$s = s_i(S, T, V, P, N, \mu) : \mathbf{R}^6 \to \mathbf{R}^3,$$

and with the property that GDP equation is a consequence of

$$\begin{aligned} s_i(S, T, V, P, N, \mu) &= 0, \\ ds_i(S, T, V, P, N, \mu) &= 0, \;\; i = \overline{1, 3}. \end{aligned}$$

Thus, a nonholonomic hypersurface in $\mathbf{R}^6$ is made of the set of all s. Moreover, the vector field $(0, S, 0, V, 0, N)$ having the field lines:

$$S = m_1, \; T = m_1 t + n_1, \; V = m_2,$$
$$P = m_2 t + n_2, \; N = m_3, \; \mu = m_3 t + n_3, \; t \in \mathbf{R},$$

where m_1, m_2, m_3 and n_1, n_2, n_3 are constants (family of straight lines), is orthogonal to the nonholonomic hypersurface.

2 Simple thermochemical systems with one state

Consider a thermochemical system of GDP type $(\mathbf{R}^6, \omega = 0)$. We want to introduce the canonical thermochemical systems with one state $c(t)$, selecting successively t as one of the 6 coordinates S, T, V, P, N, μ.

2.1. Definition. *A thermochemical system with one state $c(t)$ is called simple if the parameter state t is one of the six coordinates S, T, V, P, N,μ.*

2.2. Proposition. *There exists 6 types of simple thermochemical systems with one state.*

Between the 6 types of simple systems there exists 3 in which the state variable is measurable (the pressure P, the temperature T and the volume V).

Proof. 1) If we consider $t = S$, we will have $c(S) = (S, T(S), V(S), P(S), N(S), \mu(S))$ and the ODE (2) becomes

$$S\tfrac{dT}{dS} - V\tfrac{dP}{dS} + N\tfrac{d\mu}{dS} = 0.$$

The solution

$$T = \int \left(\frac{V}{S}\frac{dP}{dS} - \frac{N}{S}\frac{d\mu}{dS}\right) dS + C_1,$$
$$V = V(S), P = P(S), N = N(S), \mu = \mu(S)$$

of the previous ODE depends on 4 arbitrary functions of S.

2) If we take $t = T$, the integral curve is $c(T) = (S(T), T, V(T), P(T),\ N(T),\ \mu(T))$. The components of $c(T)$ verify the ODE

$$S - V\tfrac{dP}{dT} + N\tfrac{d\mu}{dT} = 0.$$

The most general solution is of the following form

$$\left(V\frac{dP}{dT} - N\frac{d\mu}{dT}, V(T), P(T), N(T), \mu(T)\right).$$

Particularly, the solutions of the form $(0, 0, P(T), 0, \mu(T))$ have a physical meaning.

2.3. Proposition. *The solutions of the form* $(0, 0, P(T), 0, \mu(T))$ *belongs to the vacuum* $N = 0$, $V = 0$.

Proof. The temperature T is measurable. The "amount" of disorder of the system (entropy) S is zero.

3) Considering $t = V$, we look for an integral curve $c(V) = (S(V), T(V), V, P(V), N(V), \mu(V))$. Its components verify the ODE

$$S\tfrac{dT}{dV} - V\tfrac{dP}{dV} + N\tfrac{d\mu}{dV} = 0.$$

The previous ODE has the solutions with components (S, T, P, N, μ) of the form

$$\left(0, T(V), \int \frac{N}{V}\frac{d\mu}{dV}dV + C_1, N(V), \mu(V)\right),$$
$$\left(S(V), C_2, \int \frac{N}{V}\frac{d\mu}{dV}dV + C_1, N(V), \mu(V)\right),$$
$$\left(\frac{N\frac{d\mu}{dV} - V\frac{dP}{dV}}{\frac{dT}{dV}}, T(V), P(V), N(V), \mu(V)\right).$$

4) $t = P$ produces an integral curve of the form $c(P) = (S(P), T(P), V(P), P, N(P), \mu(P))$. The ODE (2) becomes

$$S\frac{dT}{dP} - V + N\frac{d\mu}{dP} = 0.$$

It follows the solutions of the form

$$(0, T(P), 0, 0, \mu(P)),$$
$$\left(0, T(P), N\frac{d\mu}{dP}, N(P), \mu(P)\right),$$
$$\left(S(P), C_1, N\frac{d\mu}{dP}, N(P), \mu(P)\right),$$
$$\left(\frac{V - N\frac{d\mu}{dP}}{\frac{dT}{dP}}, V(P), N(P), \mu(P)\right).$$

5) If we consider $t = N$, the integral curve has the form $c(N) = (S(N), T(N), V(N),$. Since the components of c verify the ODE

$$S\frac{dT}{dN} - V\frac{dP}{dN} + N\frac{d\mu}{dN} = 0,$$

the solutions can be written in the form

$$(0, T(N), 0, P(N), C_1),$$
$$(0, T(N), V(N), C_1, C_2),$$
$$\left(0, T(N), N\frac{d\mu}{dN}\left(\frac{dP}{dN}\right)^{-1}, P(N), \mu(N)\right),$$
$$(S(N), C_1, V(N), C_2, C_3),$$
$$\left(S(N), C_1, N\frac{d\mu}{dN}\left(\frac{dP}{dN}\right)^{-1}, P(N), \mu(N)\right),$$
$$\left(\frac{V\frac{dP}{dN} - N\frac{d\mu}{dN}}{\frac{dT}{dN}}, T(N), V(N), P(N), \mu(N)\right).$$

6) Taking $t = \mu$, we impose an integral curve $c(\mu) = (S(\mu), T(\mu), V(\mu), P(\mu), N(\mu), \mu)$. Since the ODE (2) has the form

$$S\frac{dT}{d\mu} - V\frac{dP}{d\mu} + N = 0,$$

we obtain the solutions

$$(0, T(\mu), 0, P(\mu), 0),$$
$$(0, T(\mu), V(\mu), C_1, 0),$$
$$\left(0, T(\mu), N\left(\frac{dP}{d\mu}\right)^{-1}, P(\mu), N(\mu)\right),$$
$$(S(\mu), C_1, V(\mu), C_2, 0),$$
$$\left(S(\mu), C_1, N\left(\frac{dP}{d\mu}\right)^{-1}, P(\mu), N(\mu)\right),$$
$$\left(\left(V\frac{dP}{d\mu} - N\right)\left(\frac{dT}{d\mu}\right)^{-1}, T(\mu), V(\mu), P(\mu), N(\mu)\right).$$

3 Simple thermochemical systems with two states

Consider a thermochemical system of GDP type $(\mathbf{R}^6, \omega = 0)$. We want to introduce the canonical thermochemical systems with two states $g(x, y)$, selecting successively x and y as any two of the 6 coordinates S, T, V, P, N, μ.

3.1. Definition. *A thermochemical system with two states (x, y) is called simple if the parameter states are two of the six coordinates S, T, V, P, N,μ.*

3.2. Proposition. *There exists $C_6^2 = 15$ types of simple thermochemical system with two states.*

The simple thermochemical systems with two states are detailed in the Proof. Taking into account that the pressure P, the temperature T and the volume V are measurable, 3 of these 15 variants are essential cases with measurable state variables.

Proof. 1) Taking $x = S$, $y = T$, one gets

$$g(S, T) = (S, T, V(S, T), P(S, T), N(S, T), \mu(S, T)).$$

The PDE system (3) becomes

$$\begin{cases} -V\frac{\partial P}{\partial S} + N\frac{\partial \mu}{\partial S} = 0 \\ S - V\frac{\partial P}{\partial T} + N\frac{\partial \mu}{\partial T} = 0, \end{cases}$$

with the area condition

$$-1 + \frac{\partial V}{\partial S}\frac{\partial P}{\partial T} - \frac{\partial P}{\partial S}\frac{\partial V}{\partial T} + \frac{\partial \mu}{\partial S}\frac{\partial N}{\partial T} - \frac{\partial N}{\partial S}\frac{\partial \mu}{\partial T} = 0.$$

The solutions (V, P, N, μ) are of the form

$$\left(S\left(\frac{dP}{dT}\right)^{-1}, P(T), 0, \mu(S, T)\right),$$
$$\left(S\left(\frac{dP}{dT}\right)^{-1}, P(T), N(S, T), C_1\right),$$
$$\left(S\left(\frac{\partial P}{\partial T}\right)^{-1}, P(S, T), S\frac{\partial P}{\partial S}\left(\frac{d\mu}{dS}\frac{\partial P}{\partial T}\right)^{-1}, \mu(S)\right),$$
$$\left(V(S, T), P(T), \left(V\frac{dP}{dT} - S\right)\left(\frac{d\mu}{dT}\right)^{-1}, \mu(T)\right),$$
$$\left(0, P(S, T), -S\left(\frac{d\mu}{dT}\right)^{-1}, \mu(T)\right),$$

where C_1 is an integration constant.

2) For $x = S$ and $y = V$, we get

$$g(S, V) = (S, T(S, V), V, P(S, V), N(S, V), \mu(S, V)).$$

This integral surface verifies the PDE system

$$\begin{cases} S\frac{\partial T}{\partial S} - V\frac{\partial P}{\partial S} + N\frac{\partial \mu}{\partial S} = 0 \\ S\frac{\partial T}{\partial V} - V\frac{\partial P}{\partial V} + N\frac{\partial \mu}{\partial V} = 0, \end{cases}$$

and the area condition rewrites

$$-\frac{\partial T}{\partial V} - \frac{\partial P}{\partial S} + \frac{\partial \mu}{\partial S}\frac{\partial N}{\partial V} - \frac{\partial N}{\partial S}\frac{\partial \mu}{\partial V} = 0.$$

ISBN: 978-960-6766-50-3

ISSN: 1790-5117

One obtains the solutions (T, P, N, μ) of the form

$$\begin{gathered}(C_1, C_2, N(S), C_3)\,, \\ (C_1, C_2, N(S,V), C_3)\,, \\ (C_1, C_2, 0, \mu(S,V))\,, \\ \left(C_1, P(S), V\frac{dP}{dS}\left(\frac{d\mu}{dS}\right)^{-1}, \mu(S)\right), \\ \left(T(S), P(S), \left(V\frac{dP}{dS} - S\frac{dT}{dS}\right)\left(\frac{d\mu}{dS}\right)^{-1}, \mu(S)\right).\end{gathered}$$

3.3. Proposition. *Let $g(S,V)$ be a simple thermochemical system with two states. In the hyperplane $T(S,V) = c_1, P(S,V) = c_2, \mu(S,V) = c_3$, the number N of particles in the system is an arbitrary function of entropy (the first solution above), or of entropy and volume (the second and third solution above).*

3) $x = S$ and $y = P$ leads to

$$g(S,P) = (S, T(S,P), V(S,P), P, N(S,P), \mu(S,P)).$$

The PDE system (3) becomes

$$\begin{cases} S\frac{\partial T}{\partial S} + N\frac{\partial \mu}{\partial S} = 0 \\ S\frac{\partial T}{\partial P} - V + N\frac{\partial \mu}{\partial P} = 0, \end{cases}$$

and the area condition (4) rewrites

$$-\frac{\partial T}{\partial P} + \frac{\partial V}{\partial S} + \frac{\partial \mu}{\partial S}\frac{\partial N}{\partial P} - \frac{\partial N}{\partial S}\frac{\partial \mu}{\partial P} = 0.$$

The simplest solutions (T, V, N, μ) are of the form

$$\begin{gathered}\left(T(P), S\frac{dT}{dP}, 0, \mu(S,P)\right), \\ \left(T(P), S\frac{dT}{dP} + N\frac{d\mu}{dP}, N(S,P), \mu(P)\right), \\ \left(T(S,P), S\left(\frac{\partial T}{\partial P}\frac{\partial \mu}{\partial S} - \frac{\partial T}{\partial S}\frac{\partial \mu}{\partial P}\right)\left(\frac{\partial \mu}{\partial S}\right)^{-1}, \right. \\ \left. -S\frac{\partial T}{\partial S}\left(\frac{\partial \mu}{\partial S}\right)^{-1}, \mu(S,P)\right).\end{gathered}$$

4) If one consider the state variables $x = S$, $y = N$, it follows an integral surface

$$g(S,N)$$
$$= (S, T(S,N), V(S,N), P(S,N), N, \mu(S,P)).$$

Its components verify

$$\begin{cases} S\frac{\partial T}{\partial S} - V\frac{\partial P}{\partial S} + N\frac{\partial \mu}{\partial S} = 0 \\ S\frac{\partial T}{\partial N} - V\frac{\partial P}{\partial N} + N\frac{\partial \mu}{\partial N} = 0, \end{cases}$$

and area condition (4) becomes

$$-\frac{\partial T}{\partial N} + \frac{\partial V}{\partial S}\frac{\partial P}{\partial N} - \frac{\partial P}{\partial S}\frac{\partial V}{\partial N} + \frac{\partial \mu}{\partial S} = 0.$$

The solutions $(T, V, P\mu)$ of this PDE system are expressed by complicated relations which depend on more functions of the two state variables considered.

5) Taking $x = S$, $y = \mu$, one gets

$$g(S,\mu)$$
$$= (S, T(S,\mu), V(S,\mu), P(S,\mu), N(S,\mu), \mu).$$

The components of $g(S,\mu)$ verify the PDE system

$$\begin{cases} S\frac{\partial T}{\partial S} - V\frac{\partial P}{\partial S} = 0 \\ S\frac{\partial T}{\partial \mu} - V\frac{\partial P}{\partial \mu} + N = 0. \end{cases}$$

The area condition (4) becomes

$$-\frac{\partial T}{\partial \mu} + \frac{\partial V}{\partial S}\frac{\partial P}{\partial \mu} - \frac{\partial P}{\partial S}\frac{\partial V}{\partial \mu} - \frac{\partial N}{\partial S} = 0.$$

The solutions (T, V, P, N) of the previous PDE system can be of the form

$$\begin{gathered}\left(T(\mu), 0, P(S,\mu), -S\frac{dT}{d\mu}\right), \\ \left(T(\mu), V(S,\mu), P(\mu), V\frac{dP}{d\mu} - S\frac{dT}{d\mu}\right), \\ \left(T(S,\mu), S\frac{\partial T}{\partial S}\left(\frac{\partial P}{\partial S}\right)^{-1}, P(S,\mu), \right. \\ \left. S\left(\frac{\partial P}{\partial \mu}\frac{\partial T}{\partial S} - \frac{\partial T}{\partial \mu}\frac{\partial P}{\partial S}\right)\left(\frac{\partial P}{\partial S}\right)^{-1}\right).\end{gathered}$$

Adding the area condition, we get simpler solutions

$$\begin{gathered}(C_1, 0, P(S,\mu), 0)\,, \\ (C_1, V(S), C_2, 0)\,, \\ (C_1, V(S,\mu), C_2, 0)\,,\end{gathered}$$

where C_1 and C_2 are integration constants.

6) If we consider that the state variables are the measurable variables $x = T$ and $y = V$, the integral surface is of the form

$$g(T,V) = (S(T,V), T, V, P(T,V), N(T,V), \mu(T,V)).$$

The system (3) rewrites

$$\begin{cases} S - V\frac{\partial P}{\partial T} + N\frac{\partial \mu}{\partial T} = 0 \\ -V\frac{\partial P}{\partial V} + N\frac{\partial \mu}{\partial V} = 0, \end{cases}$$

and the area condition (4) becomes

$$\frac{\partial S}{\partial V} - \frac{\partial P}{\partial T} + \frac{\partial \mu}{\partial T}\frac{\partial N}{\partial V} - \frac{\partial N}{\partial T}\frac{\partial \mu}{\partial V} = 0.$$

The first two PDEs can have solutions (S, P, N, μ) of the form

$$\begin{gathered}\left(V\frac{dP}{dT}, P(T), 0, \mu(T,V)\right), \\ \left(-V\left(\frac{d\mu}{dT}\frac{dF}{dT} - \frac{dP}{dT}\right), P(T), VF(T), \mu(T)\right), \\ \left(-N\frac{d\mu}{dT} - V\frac{dP}{dT}, P(T), N(T,V), \mu(T)\right), \\ \left(V\left(\frac{\partial P}{\partial T}\frac{\partial \mu}{\partial V} - \frac{\partial P}{\partial V}\frac{\partial \mu}{\partial T}\right)\left(\frac{\partial \mu}{\partial V}\right)^{-1}, P(T,V), \right. \\ \left. V\frac{\partial P}{\partial V}\left(\frac{\partial \mu}{\partial V}\right)^{-1}, \mu(T,V)\right).\end{gathered}$$

Adding the area condition, we obtain the next examples of solutions

$$\begin{gathered}(0, C_1, N(T)V, C_2)\,,\\ (0, C_1, N(T,V), C_2)\,,\\ (0, C_1, 0, \mu(T,V))\,,\\ \left(0, P(T), \frac{dP}{dT}V\left(\frac{d\mu}{dT}\right)^{-1}, \mu(T)\right).\end{gathered}$$

3.4. Proposition. *Let $g(T,V)$ be a simple thermochemical system with two states. In the hyperplane $P(T,V) = c_1, \mu(T,V) = c_2$, the system has an amount of disorder equal to zero $S = 0$ (the first two solutions above).*

7) Taking $x = T$ and $y = P$, one gets $g(T,P) = (S(T,P), T, V(T,P), P, N(T,P), \mu(T,P))$. The integral surface $g(T,P)$ must verifies

$$\begin{cases} S + N\frac{\partial\mu}{\partial T} = 0 \\ -V + N\frac{\partial\mu}{\partial P} = 0, \end{cases}$$

and the equation (4) rewrites

$$\frac{\partial S}{\partial P} + \frac{\partial V}{\partial T} + \frac{\partial\mu}{\partial T}\frac{\partial N}{\partial P} - \frac{\partial N}{\partial T}\frac{\partial\mu}{\partial P} = 0.$$

This is also an essential case because the state variables T and P are measurable. The nontrivial components of a solution (S, V, N, μ) are

$$\begin{gathered}(0, 0, 0, \mu(T,P))\,,\\ \left(-N\frac{\partial\mu}{\partial T}, N\frac{\partial\mu}{\partial P}, N(T,P), \mu(T,P)\right).\end{gathered}$$

3.5. Proposition. *Let $g(T,P)$ be a simple thermochemical system described by the measurable variables temperature and the pressure. If the entropy is zero, then the integral surface models the behavior of vacuum $N = 0$ (the first solution above).*

8) For $x = T$, $y = N$, we have

$$\begin{gathered} g(T,N) \\ = (S(T,N), T, V(T,N), P(T,N), N, \mu(T,N)).\end{gathered}$$

The system (3) becomes

$$\begin{cases} S - V\frac{\partial P}{\partial T} + N\frac{\partial\mu}{\partial T} = 0 \\ -V\frac{\partial P}{\partial N} + N\frac{\partial\mu}{\partial N} = 0, \end{cases}$$

and for area condition we get

$$\frac{\partial S}{\partial N} + \frac{\partial V}{\partial T}\frac{\partial P}{\partial N} - \frac{\partial P}{\partial T}\frac{\partial V}{\partial N} + \frac{\partial\mu}{\partial T} = 0.$$

The previous PDE system can have solutions (S, V, P, μ) of the form

$$\begin{gathered}\left(-N\left(\frac{d\mu}{dT} - V\frac{dP}{dT}\right), V(T), P(T), \mu(T)\right),\\ \left(-N\left(\frac{d\mu}{dT} + V\frac{dP}{dT}\right), V(T,N), P(T), \mu(T)\right),\\ \left(N\left(\frac{\partial\mu}{\partial N}\frac{\partial P}{\partial T} - \frac{\partial\mu}{\partial T}\frac{\partial P}{\partial N}\right)\left(\frac{\partial P}{\partial N}\right)^{-1}, N\frac{\partial\mu}{\partial N}\left(\frac{\partial P}{\partial N}\right)^{-1},\right.\\ \left. P(T,N), \mu(T,N)\right).\end{gathered}$$

If we add the area condition, we get simpler solutions

$$\begin{gathered}(0, NF(T), C_1, C_2)\,,\\ (0, V(T,N), C_1, C_2)\,,\\ \left(0, N\frac{d\mu}{dT}\left(\frac{dP}{dT}\right)^{-1}, P(T), \mu(T)\right),\\ \left(F(T)\frac{dP}{dT}, T\frac{d\mu}{dT}\left(\frac{dP}{dT}\right)^{-1}, P(T), \mu(T)\right),\end{gathered}$$

depending on two integration constants C_1 and C_2.

3.6. Proposition. *Let $g(T,N)$ be a simple thermochemical system with two states. In the hyperplane $P(T,N) = c_1, \mu(T,N) = c_2$, the system has an amount of disorder equal to zero $S = 0$ (the first three solutions above).*

9) $x = T$, $y = \mu$ lead to an integral surface of the form

$$g(T,\mu) = (S(T,\mu), T, V(T,\mu), P(T,\mu), N(T,\mu), \mu).$$

The PDE system (3) becomes

$$\begin{cases} S - V\frac{\partial P}{\partial T} = 0 \\ -V\frac{\partial P}{\partial\mu} + N = 0, \end{cases}$$

and (4) rewrites

$$\frac{\partial S}{\partial\mu} + \frac{\partial V}{\partial T}\frac{\partial P}{\partial\mu} - \frac{\partial P}{\partial T}\frac{\partial V}{\partial\mu} - \frac{\partial N}{\partial T} = 0.$$

From the first two PDE we get the components (S, V, P, N) of the solutions,

$$\begin{gathered}(0, 0, P(T,\mu), 0)\,,\\ \left(V\frac{\partial P}{\partial T}, V(T,\mu), P(T,\mu), V\frac{\partial P}{\partial\mu}\right).\end{gathered}$$

Adding the area condition, we produce the solutions

$$\begin{gathered}(0, 0, P(T,\mu), 0)\,,\\ (0, V(T,\mu), C_1, 0)\,,\\ \left(V\frac{dP}{dT}, V(T), P(T), 0\right),\\ (S(T,\mu), V(T,\mu), P(T,\mu), N(T,\mu))\,.\end{gathered}$$

3.7. Proposition. *Let $g(T,\mu)$ be a simple thermochemical system with two states (the temperature and the chemical potential). If the entropy is zero, then the integral surface models the behavior of vacuum $(N = 0)$ (the first two solutions above).*

10) Again measurable variables $x = V$, $y = P$, i.e., an integral surface of the form

$$g(V,P) = (S(V,P), T(V,P), V, P, N(V,P), \mu(V,P)),$$

where

$$\begin{cases} S\frac{\partial T}{\partial V} + N\frac{\partial\mu}{\partial V} = 0 \\ S\frac{\partial T}{\partial P} - V + N\frac{\partial\mu}{\partial P} = 0. \end{cases}$$

The components also verify the area condition

$$\frac{\partial T}{\partial V}\frac{\partial S}{\partial P} - \frac{\partial S}{\partial V}\frac{\partial T}{\partial P} + 1 + \frac{\partial \mu}{\partial V}\frac{\partial N}{\partial P} - \frac{\partial N}{\partial V}\frac{\partial \mu}{\partial P} = 0.$$

The form of solutions (S, T, N, μ) is

$$\begin{gathered}\left(V\left(\frac{dT}{dP}\right)^{-1}, T(P), 0, \mu(V,P)\right),\\ \left(V\left(\frac{dT}{dP}\right)^{-1}, T(P), N(V,P), C_1\right),\\ \left(V\left(\frac{\partial T}{\partial P}\right), T(V,P), -V\frac{\partial T}{\partial V}\left(\frac{d\mu}{dV}\frac{\partial T}{\partial P}\right), \mu(V)\right),\\ \left(S(V,P), T(P), \left(V - S\frac{dT}{dP}\right)\left(\frac{d\mu}{dP}\right)^{-1}, \mu(P)\right).\end{gathered}$$

Adding the area condition, we find

$$\begin{gathered}\left(V\left(\frac{dT}{dP}\right)^{-1}, T(P), 0, \mu(V,P)\right),\\ \left(S(V), c_1, V\left(\frac{d\mu}{dP}\right)^{-1}, \mu(P)\right),\\ \left(-Vc_4\left(c_2\frac{dT}{dV}\left(2c_4V + c_1\right)\right)^{-1}, T(V),\right.\\ \left. V\left(c_3c_2e^{c_2P}\sqrt{2c_4V + c_1}\right)^{-1}, c_3e^{c_2P}\sqrt{2c_4V + c_1}\right),\end{gathered}$$

where c_1, c_2, c_3, c_4 are integration constants.

3.8. Proposition. *Let $g(V,P)$ be a simple thermochemical system with two states (the measurable variables volume and the pressure). If the temperature depends only on volume, then the thermochemical system does not depend on pressure but only on volume (the third solution above).*

11) If V and N are taken as state variables, one obtains

$$g(V,N) = (S(V,N), T(V,N), V, P(V,N), N, \mu(V,N))$$

as possible integral surface. The system (3) has the form

$$\begin{cases} S\frac{\partial T}{\partial V} - V\frac{\partial P}{\partial V} + N\frac{\partial \mu}{\partial V} = 0\\ S\frac{\partial T}{\partial N} - V\frac{\partial P}{\partial N} + N\frac{\partial \mu}{\partial N} = 0,\end{cases}$$

and (4) becomes

$$\frac{\partial T}{\partial V}\frac{\partial S}{\partial N} - \frac{\partial S}{\partial V}\frac{\partial T}{\partial N} + \frac{\partial P}{\partial N} + \frac{\partial \mu}{\partial V} = 0.$$

The general solution has complicated form. The simplest case is of the form

$$S = S(V,N), T = C_1, P = P\left(\frac{N}{V}\right),$$
$$\mu = \int \frac{1}{N}\frac{dP}{d\left(\frac{N}{V}\right)}dN + C_2.$$

12) If we consider the state variables $x = V$ and $y = \mu$, we get a candidate

$$g(V,\mu) = (S(V,\mu), T(V,\mu), V, P(V,\mu), N(V,\mu), \mu).$$

for an integral surface. The PDE system (3) rewrites

$$\begin{cases} S\frac{\partial T}{\partial V} - V\frac{\partial P}{\partial V} = 0\\ S\frac{\partial T}{\partial \mu} - V\frac{\partial P}{\partial \mu} + N = 0,\end{cases}$$

and PDE (4) is now

$$\frac{\partial T}{\partial V}\frac{\partial S}{\partial \mu} - \frac{\partial S}{\partial V}\frac{\partial T}{\partial \mu} + \frac{\partial P}{\partial \mu} - \frac{\partial N}{\partial V} = 0.$$

The solutions are represented by the components (S, T, P, N):

$$\begin{gathered}\left(S(V,\mu), T(\mu), P(\mu), -S\frac{dT}{d\mu} + V\frac{dP}{d\mu}\right),\\ \left(V\frac{\partial P}{\partial V}\left(\frac{\partial T}{\partial V}\right)^{-1}, T(V,\mu), P(V,\mu),\right.\\ \left.-V\left(\frac{\partial P}{\partial V}\frac{\partial T}{\partial \mu} - \frac{\partial P}{\partial \mu}\frac{\partial T}{\partial V}\right)\left(\frac{\partial T}{\partial V}\right)^{-1}\right).\end{gathered}$$

13) Considering $x = P$, $y = N$, one obtains

$$g(P,N) = (S(P,N), T(P,N), V(P,N), P, N, \mu(P,N)).$$

The components of this integral surface verify the PDE system

$$\begin{cases} S\frac{\partial T}{\partial P} - V + N\frac{\partial \mu}{\partial P} = 0\\ S\frac{\partial T}{\partial N} + N\frac{\partial \mu}{\partial N} = 0,\end{cases}$$

with the area condition

$$\frac{\partial T}{\partial P}\frac{\partial S}{\partial N} - \frac{\partial S}{\partial P}\frac{\partial T}{\partial N} - \frac{\partial V}{\partial N} + \frac{\partial \mu}{\partial P} = 0.$$

It follows the solutions via the components (S, T, V, μ):

$$\begin{gathered}\left(F(P)N, T(P), N\left(\frac{d\mu}{dP} + \frac{dF}{dP}\frac{dT}{dP}\right), \mu(P)\right),\\ \left(S(P,N), T(P), N\frac{d\mu}{dP} + S\frac{dT}{dP}, \mu(P)\right),\\ \left(-N\frac{\partial \mu}{\partial N}\left(\frac{\partial T}{\partial N}\right)^{-1}, T(P,N),\right.\\ \left.-N\left(\frac{\partial \mu}{\partial N}\frac{\partial T}{\partial P} - \frac{\partial \mu}{\partial P}\frac{\partial T}{\partial N}\right)\left(\frac{\partial T}{\partial N}\right)^{-1}, \mu(P,N)\right),\end{gathered}$$

where $F(P)$ is an arbitrary function of P.

14) Taking $x = P$, $y = \mu$, i.e.,

$$g(P,\mu) = (S(P,\mu), T(P,\mu), V(P,\mu), P, N(P,\mu), \mu),$$

the PDE system (3) takes the form

$$\begin{cases} S\frac{\partial T}{\partial P} - V = 0\\ S\frac{\partial T}{\partial \mu} + N = 0,\end{cases}$$

and equation (4) becomes

$$\frac{\partial T}{\partial P}\frac{\partial S}{\partial \mu} - \frac{\partial S}{\partial P}\frac{\partial T}{\partial \mu} - \frac{\partial V}{\partial \mu} - \frac{\partial N}{\partial P} = 0.$$

This PDE system has solutions of the form

$$\begin{gathered}(0, T(P,\mu), 0, 0)\,,\\ \left(S(P,\mu), T(P), S\tfrac{dT}{dP}, 0\right),\\ \left(-N\left(\tfrac{\partial T}{\partial \mu}\right), T(P,\mu), -N\tfrac{\partial T}{\partial P}\left(\tfrac{\partial T}{\partial \mu}\right)^{-1}, N(\mu)\right).\end{gathered}$$

3.9. Proposition. *Let $g(P,\mu)$ be a simple thermochemical system with two states (the pressure and the chemical potential). If the entropy is zero, then the integral surface models the behavior of vacuum ($N = 0$) (the first solution above).*

15) Taking $x = N$, $y = \mu$, one gets

$$g(N,\mu)$$

$$= (S(N,\mu), T(N,\mu), V(N,\mu), P(N,\mu), N, \mu).$$

The PDE system (3) becomes

$$\begin{cases} S\frac{\partial T}{\partial N} - V\frac{\partial P}{\partial N} = 0 \\ S\frac{\partial T}{\partial \mu} - V\frac{\partial P}{\partial \mu} + N = 0, \end{cases}$$

and (4) is now

$$\frac{\partial T}{\partial N}\frac{\partial S}{\partial \mu} - \frac{\partial S}{\partial N}\frac{\partial T}{\partial \mu} + \frac{\partial V}{\partial N}\frac{\partial P}{\partial \mu} - \frac{\partial P}{\partial N}\frac{\partial V}{\partial \mu} - 1 = 0.$$

We can start with solutions of the form (S,T,V,P), where

$$\begin{gathered}\left(0, T(N,\mu), N\left(\tfrac{dP}{d\mu}\right)^{-1}, P(\mu)\right),\\ \left(-N\left(\tfrac{dT}{d\mu}\right)^{-1}, T(\mu), V(N,\mu), C_1\right),\\ \left(S(N,\mu), T(\mu), \left(S\tfrac{dT}{d\mu} + N\right)\left(\tfrac{dP}{d\mu}\right)^{-1}, P(\mu)\right).\end{gathered}$$

The area condition select the solutions

$$\begin{gathered}\left(\tfrac{1}{2}\left(2\tfrac{dF_2}{dN}\sqrt{N} + F_1(\mu)\right)\left(\tfrac{dF_1}{d\mu}\tfrac{dT}{dN}\right)^{-1}, T(N),\right.\\ \left.\sqrt{N}\left(\tfrac{dF_1}{d\mu}\right)^{-1}, F_2(N) + F_1(\mu)\right),\\ \left(-\tfrac{1}{2}\left(N - 2\tfrac{dP}{d\mu}F_1(\mu)\right), T(\mu),\right.\\ \left.\tfrac{1}{2}N\left(\tfrac{dP}{d\mu}\right)^{-1} + F_1(\mu), P(\mu)\right),\end{gathered}$$

where F_1 is an arbitrary function of μ and F_2 is an arbitrary function of N.

4 Simple thermochemical systems with three states

Consider a thermochemical system of GDP type $(\mathbf{R}^6, \omega = 0)$. We want to introduce the canonical thermochemical systems with three states $s(x,y,z)$, selecting successively x, y and z as three of the 6 coordinates S, T, V, P, N, μ.

4.1. Definition. *A thermochemical system with three states (x,y,z) is called simple if the parameter states are three of the six coordinates S, T, V, P, N,μ.*

4.2. Proposition. *There exists $C_6^3 = 20$ types of simple thermochemical system with three states.*

Taking into account that the pressure P, the temperature T and the volume V are measurable, one of these 20 variants is an essential case with measurable state variables.

Proof. 1) For $x = S$, $y = T$, $z = V$, we have an integral hypersurface of the form

$$s(S,T,V)$$

$$= (S, T, V, P(S,T,V), N(S,T,V), \mu(S,T,V)),$$

solution of the PDE system (5), i.e.,

$$\begin{cases} -V\frac{\partial P}{\partial S} + N\frac{\partial \mu}{\partial S} = 0 \\ S - V\frac{\partial P}{\partial T} + N\frac{\partial \mu}{\partial T} = 0 \\ -V\frac{\partial P}{\partial V} + N\frac{\partial \mu}{\partial V} = 0, \end{cases}$$

and the area relations (6) rewrites

$$\begin{cases} \frac{\partial N}{\partial T}\frac{\partial \mu}{\partial S} - 1 - \frac{\partial N}{\partial S}\frac{\partial \mu}{\partial T} = 0 \\ -\frac{\partial P}{\partial S} + \frac{\partial N}{\partial V}\frac{\partial \mu}{\partial S} - \frac{\partial N}{\partial S}\frac{\partial \mu}{\partial V} = 0 \\ -\frac{\partial P}{\partial T} + \frac{\partial N}{\partial V}\frac{\partial \mu}{\partial T} - \frac{\partial N}{\partial T}\frac{\partial \mu}{\partial V} = 0. \end{cases}$$

One simple solution of this PDE system is of the form

$$\begin{gathered}P = P(T)\,,\\ N = \left(-S + V\tfrac{dP}{dT}\right)\left(\tfrac{d\mu}{dT}\right)^{-1},\\ \mu = \mu(T)\,,\end{gathered}$$

where P and μ are arbitrary functions of T.

More precisely, one gets a nice solution which depend on four integration constants.

4.3. Theorem. *A simple thermochemical system $s(S,T,V)$, with three states (the entropy, the temperature and the volume), has the components*

$$\begin{gathered}P = \tfrac{TS}{V} + C_2C_3\tfrac{S}{V} + C_4,\\ N = VT\tfrac{1}{C_2} + C_3V,\\ \mu = C_2\tfrac{S}{V} + C_1.\end{gathered}$$

2) If we take $x = S$, $y = T$, and $z = P$, i.e,

$$s(S,T,P)$$

$$= (S, T, V(S,T,P), P, N(S,T,P), \mu(S,T,P)),$$

the PDE system (5) becomes

$$\begin{cases} N\frac{\partial \mu}{\partial S} = 0 \\ S + N\frac{\partial \mu}{\partial T} = 0 \\ -V + N\frac{\partial \mu}{\partial P} = 0, \end{cases}$$

and the area relations (6) rewrites

$$\left\{\begin{array}{l} \frac{\partial N}{\partial T}\frac{\partial \mu}{\partial S} - 1 - \frac{\partial N}{\partial S}\frac{\partial \mu}{\partial T} = 0 \\ \frac{\partial N}{\partial P}\frac{\partial \mu}{\partial S} + \frac{\partial V}{\partial S} - \frac{\partial N}{\partial S}\frac{\partial \mu}{\partial P} = 0 \\ \frac{\partial N}{\partial P}\frac{\partial \mu}{\partial T} + \frac{\partial V}{\partial T} - \frac{\partial N}{\partial T}\frac{\partial \mu}{\partial P} = 0. \end{array}\right.$$

These PDEs have solutions of the form

$$\begin{array}{c} V = -S\left(\frac{\partial \mu}{\partial P}\right)\left(\frac{\partial \mu}{\partial T}\right)^{-1}, \\ N = -S\left(\frac{\partial \mu}{\partial T}\right)^{-1}, \\ \mu = \mu(T, P). \end{array}$$

Here μ is an arbitrary function of T and P.

3) When the state variables are $x = S$, $y = T$ and $z = N$, the resulting integral hypersurface must have the form

$$s(S, T, N)$$

$$= (S, T, V(S, T, N), P(S, T, N), N, \mu(S, T, N)).$$

The PDE system (5) becomes

$$\left\{\begin{array}{l} -V\frac{\partial P}{\partial S} + N\frac{\partial \mu}{\partial S} = 0 \\ S - V\frac{\partial P}{\partial T} + N\frac{\partial \mu}{\partial T} = 0 \\ -V\frac{\partial P}{\partial N} + N\frac{\partial \mu}{\partial N} = 0, \end{array}\right.$$

and the PDE system (6) rewrites

$$\left\{\begin{array}{l} -\frac{\partial V}{\partial T}\frac{\partial P}{\partial S} - 1 + \frac{\partial V}{\partial S}\frac{\partial P}{\partial T} = 0 \\ -\frac{\partial V}{\partial N}\frac{\partial P}{\partial S} + \frac{\partial \mu}{\partial S} + \frac{\partial V}{\partial S}\frac{\partial P}{\partial N} = 0 \\ -\frac{\partial V}{\partial N}\frac{\partial P}{\partial T} + \frac{\partial \mu}{\partial T} + \frac{\partial V}{\partial T}\frac{\partial P}{\partial N} = 0. \end{array}\right.$$

This PDE system (5)+(6) has complicated solutions. A simple example of solution is

$$\begin{array}{c} V = \left(S + F(T)N\frac{dP}{dT}\right)\left(\frac{dP}{dT}\right)^{-1}, \\ P = P(T), \\ \mu = \int F(T)\frac{dP}{dT}dT + C_1, \end{array}$$

in which P and F are two arbitrary functions of T .

4) Let now consider the state variables $x = S$, $y = T$, $z = \mu$. In this case we have

$$s(S, T, \mu)$$

$$= (S, T, V(S, T, \mu), P(S, T, \mu), N(S, T, \mu), \mu)$$

must verifies the PDE system

$$\left\{\begin{array}{l} -V\frac{\partial P}{\partial S} = 0 \\ S - V\frac{\partial P}{\partial T} = 0 \\ -V\frac{\partial P}{\partial \mu} + N = 0. \end{array}\right.$$

and the area conditions (7),

$$\left\{\begin{array}{l} -\frac{\partial V}{\partial T}\frac{\partial P}{\partial S} - 1 + \frac{\partial V}{\partial S}\frac{\partial P}{\partial T} = 0 \\ -\frac{\partial V}{\partial \mu}\frac{\partial P}{\partial S} + \frac{\partial V}{\partial S}\frac{\partial P}{\partial \mu} - \frac{\partial N}{\partial S} = 0 \\ -\frac{\partial V}{\partial \mu}\frac{\partial P}{\partial T} + \frac{\partial V}{\partial T}\frac{\partial P}{\partial \mu} - \frac{\partial N}{\partial T} = 0. \end{array}\right.$$

The solutions are of the form

$$\begin{array}{c} V = S\left(\frac{\partial P}{\partial T}\right)^{-1}, \\ P = P(T, \mu), \\ N = -S\left(\frac{\partial P}{\partial \mu}\right)\left(\frac{\partial P}{\partial T}\right)^{-1}. \end{array}$$

5) Now, let us take the states variables $x = S$, $y = V$, $z = P$. The integral hypersurface

$$s(S, V, P)$$

$$= (S, T(S, V, P), V, P, N(S, V, P), \mu(S, V, P))$$

is a solution of the PDE system (5)+(6), i.e.,

$$\left\{\begin{array}{l} S\frac{\partial T}{\partial S} + N\frac{\partial \mu}{\partial S} = 0 \\ S\frac{\partial T}{\partial V} + N\frac{\partial \mu}{\partial V} = 0 \\ S\frac{\partial T}{\partial P} - V + N\frac{\partial \mu}{\partial P} = 0, \end{array}\right.$$

$$\left\{\begin{array}{l} \frac{\partial N}{\partial V}\frac{\partial \mu}{\partial S} - \frac{\partial T}{\partial V} - \frac{\partial N}{\partial S}\frac{\partial \mu}{\partial V} = 0 \\ \frac{\partial N}{\partial P}\frac{\partial \mu}{\partial S} - \frac{\partial T}{\partial P} - \frac{\partial N}{\partial S}\frac{\partial \mu}{\partial P} = 0 \\ \frac{\partial N}{\partial P}\frac{\partial \mu}{\partial V} + 1 - \frac{\partial N}{\partial V}\frac{\partial \mu}{\partial P} = 0. \end{array}\right.$$

The simplest solution for the first three PDE system is

$$\begin{array}{c} T = T(P), \\ N = \left(V - S\frac{dT}{dP}\right)\left(\frac{d\mu}{dP}\right)^{-1}, \\ \mu = \mu(P), \end{array}$$

where T and μ are arbitrary functions of P determined by the second PDE system.

6) If we take $x = S$, $y = V$ and $z = N$ or

$$s(S, V, N)$$

$$= (S, T(S, V, N), V, P(S, V, N), N, \mu(S, V, N)),$$

then the PDE system (5) becomes

$$\left\{\begin{array}{l} S\frac{\partial T}{\partial S} - V\frac{\partial P}{\partial S} + N\frac{\partial \mu}{\partial S} = 0 \\ S\frac{\partial T}{\partial V} - V\frac{\partial P}{\partial V} + N\frac{\partial \mu}{\partial V} = 0 \\ S\frac{\partial T}{\partial N} - V\frac{\partial P}{\partial N} + N\frac{\partial \mu}{\partial N} = 0. \end{array}\right.$$

The area relations (6) can be written in the following form

$$\left\{\begin{array}{l} -\frac{\partial P}{\partial S} - \frac{\partial T}{\partial V} = 0 \\ \frac{\partial \mu}{\partial S} - \frac{\partial T}{\partial N} = 0 \\ \frac{\partial \mu}{\partial V} + \frac{\partial P}{\partial N} = 0. \end{array}\right.$$

Looking for the solutions of these PDEs, one obtains complicated expressions.

7) If the considered state variables are $x = S$, $y = V$, $z = \mu$ then

$$s(S, V, \mu)$$

$$= (S, T(S,V,\mu), V, P(S,V,\mu), N(S,V,\mu), \mu),$$

must verify the PDE system

$$\begin{cases} S\frac{\partial T}{\partial S} - V\frac{\partial P}{\partial S} = 0 \\ S\frac{\partial T}{\partial V} - V\frac{\partial P}{\partial V} = 0 \\ S\frac{\partial T}{\partial \mu} - V\frac{\partial P}{\partial \mu} + N = 0, \end{cases}$$

and the area conditions

$$\begin{cases} -\frac{\partial P}{\partial S} - \frac{\partial T}{\partial V} = 0 \\ -\frac{\partial T}{\partial \mu} - \frac{\partial N}{\partial S} = 0 \\ +\frac{\partial P}{\partial \mu} - \frac{\partial N}{\partial V} = 0. \end{cases}$$

Open problem. Find the general solution.

8) Getting S, P, N as state variables and

$$s(S,P,N) = (S, T(S,P,N), V(S,P,N), P, N, \mu(S,P,N))$$

as integral hypersurface the PDE system (5), we must have

$$\begin{cases} S\frac{\partial T}{\partial S} + N\frac{\partial \mu}{\partial S} = 0 \\ S\frac{\partial T}{\partial P} - V + N\frac{\partial \mu}{\partial P} = 0 \\ S\frac{\partial T}{\partial N} + N\frac{\partial \mu}{\partial N} = 0. \end{cases}$$

The PDE system (6) will be written in the form

$$\begin{cases} -\frac{\partial T}{\partial P} + \frac{\partial V}{\partial S} = 0 \\ +\frac{\partial \mu}{\partial S} - \frac{\partial T}{\partial N} = 0 \\ -\frac{\partial V}{\partial N} + \frac{\partial \mu}{\partial P} = 0. \end{cases}$$

Open problem. Find the general solution.

9) Let consider the state variables $x = S$, $y = P$, $z = \mu$. Then

$$s(S,P,\mu)$$

$$= (S, T(S,P,\mu), V(S,P,\mu), P, N(S,P,\mu), \mu),$$

must be solution of the PDE system (5)

$$\begin{cases} S\frac{\partial T}{\partial S} = 0 \\ S\frac{\partial T}{\partial P} - V = 0 \\ S\frac{\partial T}{\partial \mu} + N = 0, \end{cases}$$

and of PDE system (6)

$$\begin{cases} -\frac{\partial T}{\partial P} + \frac{\partial V}{\partial S} = 0 \\ -\frac{\partial T}{\partial \mu} - \frac{\partial N}{\partial S} = 0 \\ -\frac{\partial V}{\partial \mu} - \frac{\partial N}{\partial P} = 0. \end{cases}$$

It follows

$$\left(T = T(P,\mu), V = S\frac{\partial T}{\partial P}, N = -S\frac{\partial T}{\partial \mu}\right),$$

where T is an arbitrary function of two state variables P and μ.

10) If $x = S$, $y = N$, $z = \mu$, one looks for

$$s(S,N,\mu)$$

$$= (S, T(S,N,\mu), V(S,N,\mu), P(S,N,\mu), N, \mu).$$

In this case (5) becomes

$$\begin{cases} S\frac{\partial T}{\partial S} - V\frac{\partial P}{\partial S} = 0 \\ S\frac{\partial T}{\partial N} - V\frac{\partial P}{\partial N} = 0 \\ S\frac{\partial T}{\partial \mu} - V\frac{\partial P}{\partial \mu} + N = 0. \end{cases}$$

For the PDE system (6), we get

$$\begin{cases} -\frac{\partial V}{\partial N}\frac{\partial P}{\partial S} - \frac{\partial T}{\partial N} + \frac{\partial V}{\partial S}\frac{\partial P}{\partial N} = 0 \\ -\frac{\partial V}{\partial \mu}\frac{\partial P}{\partial S} - \frac{\partial T}{\partial \mu} + \frac{\partial V}{\partial S}\frac{\partial P}{\partial \mu} = 0 \\ -\frac{\partial V}{\partial \mu}\frac{\partial P}{\partial N} + \frac{\partial V}{\partial N}\frac{\partial P}{\partial \mu} - 1 = 0. \end{cases}$$

A simple solution of the first three PDEs can be of the form

$$T = T(\mu),$$
$$V = \left(S\frac{dT}{d\mu} + N\right)\left(\frac{dP}{d\mu}\right)^{-1},$$
$$P = P(\mu),$$

where T and P are arbitrary functions of the state variable μ. Adding the other three PDEs, we obtain two very nice solutions. One of these depends on four integration constants, and a second one depends on 5 integration constants.

4.4. Theorem. *The most general simple thermochemical system of the form $s(S,N,\mu)$ has the components*

$$T = -\frac{\mu N}{S} - C_2C_3\frac{N}{S} + C_4,$$
$$V = \frac{1}{C_2}N\mu + C_3N,$$
$$P = C_1 + C_2\ln S - c_2\ln N,$$

or

$$V = \frac{N(C_2-1)(C_3\mu+C_4)}{C_1C_2C_3}\left(\frac{C_2}{(C_3\mu+C_4)(C_2-1)}\right)^{-\frac{C_2}{C_2-1}},$$
$$T = \frac{C_2N(C_3\mu+C_4)}{SC_3C_1}\left(\frac{N}{S}\right)^{-C_2} + C_5,$$
$$P = \left(\frac{C_2}{(C_3\mu+C_4)(C_2-1)}\right)^{\frac{C_2}{C_2-1}}\left(C_1 + C_2\left(\frac{N}{S}\right)^{-C_2}\right).$$

11) Getting T, V, P as state variables, the integral hypersurface is of the form

$$s(T,V,P)$$

$$= (S(T,V,P), T, V, P, N(T,V,P), \mu(T,V,P)).$$

The PDE system (5) is written

$$\begin{cases} S + N\frac{\partial \mu}{\partial T} = 0 \\ N\frac{\partial \mu}{\partial V} = 0 \\ -V + N\frac{\partial \mu}{\partial P} = 0, \end{cases}$$

and the area conditions (6) can be put in the following form

$$\begin{cases} \frac{\partial S}{\partial V} + \frac{\partial N}{\partial V}\frac{\partial \mu}{\partial T} - \frac{\partial N}{\partial T}\frac{\partial \mu}{\partial V} = 0 \\ \frac{\partial S}{\partial P} + \frac{\partial N}{\partial P}\frac{\partial \mu}{\partial T} - \frac{\partial N}{\partial T}\frac{\partial \mu}{\partial Pz} = 0 \\ \frac{\partial N}{\partial P}\frac{\partial \mu}{\partial V} + 1 - \frac{\partial N}{\partial V}\frac{\partial \mu}{\partial P} = 0. \end{cases}$$

The general solution has the form

$$S = -V\left(\frac{\partial \mu}{\partial P}\right)^{-1}\left(\frac{\partial \mu}{\partial T}\right),$$
$$N = V\left(\frac{\partial \mu}{\partial P}\right)^{-1},$$
$$\mu = \mu(T, P),$$

where $\mu(T, P)$ is an arbitrary function of two state variables. This model is very important for applications because all the state variables are measurable.

4.5. Theorem. *If the state variables are T, V, P, then the corresponding simple thermochemical system is determined only by a chemical potential μ as an arbitrary function of temperature T and pressure P.*

12) If we consider $x = T$, $y = V$, $z = N$, i.e.,

$$s(T, V, N)$$
$$= (S(T, V, N), T, V, P(T, V, N), N, \mu(T, V, N)),$$

then the system (5) can be written

$$\begin{cases} S - V\frac{\partial P}{\partial T} + N\frac{\partial \mu}{\partial T} = 0 \\ -V\frac{\partial P}{\partial V} + N\frac{\partial \mu}{\partial V} = 0 \\ -V\frac{\partial P}{\partial N} + N\frac{\partial \mu}{\partial N} = 0, \end{cases}$$

and (6) will be

$$\begin{cases} \frac{\partial S}{\partial V} - \frac{\partial P}{\partial T} = 0 \\ \frac{\partial S}{\partial N} + \frac{\partial \mu}{\partial T} = 0 \\ \frac{\partial \mu}{\partial V} + \frac{\partial P}{\partial N} = 0. \end{cases}$$

Open problem. Find the general solution.

13) Let us consider $x = T$, $y = V$, $z = \mu$. The integral hypersurface

$$s(T, V, \mu)$$
$$= (S(T, V, \mu), T, V, P(T, V, \mu), N(T, V, \mu), \mu)$$

must be solution of the PDE system (5),

$$\begin{cases} S - V\frac{\partial P}{\partial T} = 0 \\ -V\frac{\partial P}{\partial V} = 0 \\ -V\frac{\partial P}{\partial \mu} + N = 0, \end{cases}$$

and the PDE system (6),

$$\begin{cases} \frac{\partial S}{\partial V} - \frac{\partial P}{\partial T} = 0 \\ \frac{\partial S}{\partial \mu} - \frac{\partial N}{\partial T} = 0 \\ +\frac{\partial P}{\partial \mu} - \frac{\partial N}{\partial V} = 0. \end{cases}$$

We get the solution

$$S = V\left(\frac{\partial P}{\partial T}\right), P = P(T, \mu), N = V\left(\frac{\partial P}{\partial \mu}\right),$$

where $P(T, \mu)$ is an arbitrary function.

14) When the state variables $x = T$, $y = P$, $z = N$ are considered, one gets

$$s(T, P, N)$$
$$= (S(T, P, N), T, V(T, P, N), P, N, \mu(T, P, N)).$$

The components of this hypersurface verify the PDE system

$$\begin{cases} S + N\frac{\partial \mu}{\partial T} = 0 \\ -V + N\frac{\partial \mu}{\partial P} = 0 \\ N\frac{\partial \mu}{\partial N} = 0, \end{cases}$$

and the area conditions become

$$\begin{cases} \frac{\partial S}{\partial P} + \frac{\partial V}{\partial T} = 0 \\ \frac{\partial S}{\partial N} + \frac{\partial \mu}{\partial T} = 0 \\ -\frac{\partial V}{\partial N} + \frac{\partial \mu}{\partial P} = 0. \end{cases}$$

The PDE system (5)+(6) has the solution

$$S = -N\left(\frac{\partial \mu}{\partial T}\right), V = N\left(\frac{\partial \mu}{\partial P}\right), \mu = \mu(T, P),$$

in which μ is an arbitrary function of T and P.

15) Let us take $x = T$, $y = P$, $z = \mu$ for the state variables. This leads to

$$s(T, P, \mu)$$
$$= (S(T, P, \mu), T, V(T, P, \mu), P, N(T, P, \mu), \mu),$$

and the PDE system (5) ca be written

$$\begin{cases} S = 0 \\ -V = 0 \\ N = 0. \end{cases}$$

The area relations (6) rewrite

$$\begin{cases} \frac{\partial S}{\partial P} + \frac{\partial V}{\partial T} = 0 \\ \frac{\partial S}{\partial \mu} - \frac{\partial N}{\partial T} = 0 \\ -\frac{\partial V}{\partial \mu} - \frac{\partial N}{\partial P} = 0. \end{cases}$$

In this case the integral manifold is an hyperplane of dimension 3,

$$s(T, P, \mu) = (0, T, 0, P, 0, \mu).$$

4.6. Theorem. *If the states are the temperature, the pressure and the chemical potential, then the integral hypersurface of dimension 3 is a hyperplane. It models the behavior of vacuum $N = 0$.*

16) If we consider the state variables $x = T$, $y = N$ and $z = \mu$, we get the hypersurface

$$s(T, N, \mu)$$
$$= (S(T, N, \mu), T, V(T, N, \mu), P(T, N, \mu), N, \mu).$$

The PDE system (5) becomes

$$\begin{cases} S - V\frac{\partial P}{\partial T} = 0 \\ -V\frac{\partial P}{\partial N} = 0 \\ -V\frac{\partial P}{\partial \mu} + N = 0, \end{cases}$$

and the PDE system (6) will be

$$\begin{cases} \frac{\partial S}{\partial N} - \frac{\partial V}{\partial N}\frac{\partial P}{\partial T} + \frac{\partial V}{\partial T}\frac{\partial P}{\partial N} = 0 \\ \frac{\partial S}{\partial \mu} - \frac{\partial V}{\partial \mu}\frac{\partial P}{\partial T} + \frac{\partial V}{\partial T}\frac{\partial P}{\partial \mu} = 0 \\ -\frac{\partial V}{\partial \mu}\frac{\partial P}{\partial N} + \frac{\partial V}{\partial N}\frac{\partial P}{\partial \mu} - 1 = 0. \end{cases}$$

The general solution is of the form

$$S = N\left(\frac{\partial P}{\partial \mu}\right)^{-1}\left(\frac{\partial P}{\partial T}\right),$$
$$V = N\left(\frac{\partial P}{\partial \mu}\right)^{-1},$$
$$P = P(T, \mu),$$

where $P(T, \mu)$ is an arbitrary function.

17) When the state variables $x = V$, $y = P$, $z = N$ are considered, i.e.,

$$s(V, P, N)$$
$$= (S(V, P, N), T(V, P, N), V, P, N, \mu(V, P, N)),$$

the PDE system (5) will be

$$\begin{cases} S\frac{\partial T}{\partial V} + N\frac{\partial \mu}{\partial V} = 0 \\ S\frac{\partial T}{\partial P} - V + N\frac{\partial \mu}{\partial P} = 0 \\ S\frac{\partial T}{\partial N} + N\frac{\partial \mu}{\partial N} = 0. \end{cases}$$

and the PDE system (6)

$$\begin{cases} \frac{\partial S}{\partial P}\frac{\partial T}{\partial V} - \frac{\partial S}{\partial V}\frac{\partial T}{\partial P} + 1 = 0 \\ \frac{\partial S}{\partial N}\frac{\partial T}{\partial V} + \frac{\partial \mu}{\partial V} - \frac{\partial S}{\partial V}\frac{\partial T}{\partial N} = 0 \\ \frac{\partial S}{\partial N}\frac{\partial T}{\partial P} + \frac{\partial \mu}{\partial P} - \frac{\partial S}{\partial P}\frac{\partial T}{\partial N} = 0. \end{cases}$$

For the first three PDEs, a simple solution is

$$S = \left(-N\frac{d\mu}{dP} + V\right)\left(\frac{dT}{dP}\right)^{-1},$$
$$T = T(P),$$
$$\mu = \mu(P),$$

where $\mu(P)$ and $T(P)$ are arbitrary functions. Between the solutions of the system made by all the six PDEs, the simplest one is

$$S = \left(V + F(P)N\frac{dT}{dP}\right)\left(\frac{dT}{dP}\right)^{-1},$$
$$T = T(P),$$
$$\mu = \int -F(P)TdP + C_1),$$

where $F(P)$ and $T(P)$ are arbitrary functions of state variable P.

18) For V, P, μ as state variables, i.e.,

$$s(V, P, \mu)$$
$$= (S(V, P, \mu), T(V, P, \mu), V, P, N(V, P, \mu), \mu),$$

the PDE system (5) will be written

$$\begin{cases} S\frac{\partial T}{\partial V} = 0 \\ S\frac{\partial T}{\partial P} - V = 0 \\ S\frac{\partial T}{\partial \mu} + N = 0. \end{cases}$$

The PDE system (6) is

$$\begin{cases} \frac{\partial S}{\partial P}\frac{\partial T}{\partial V} - \frac{\partial S}{\partial V}\frac{\partial T}{\partial P} + 1 = 0 \\ \frac{\partial S}{\partial \mu}\frac{\partial T}{\partial V} - \frac{\partial S}{\partial V}\frac{\partial T}{\partial \mu} - \frac{\partial N}{\partial V} = 0 \\ \frac{\partial S}{\partial \mu}\frac{\partial T}{\partial P} - \frac{\partial S}{\partial P}\frac{\partial T}{\partial \mu} - \frac{\partial N}{\partial P} = 0. \end{cases}$$

Here we can have a solution

$$S = V\left(\frac{\partial T}{\partial P}\right)^{-1},$$
$$T = T(P, \mu),$$
$$N = -V\left(\frac{\partial T}{\partial P}\right)^{-1}\left(\frac{\partial T}{\partial \mu}\right),$$

where the arbitrary function T is fixed by the PDE system (6).

19) For $x = V$, $y = N$ and $z = \mu$, an integral hypersurface will be

$$s(V, N, \mu)$$
$$= (S(V, N, \mu), T(V, N, \mu), V, P(V, N, \mu), N, \mu).$$

The components of the previous integral hypersurface must verify the PDEs

$$\begin{cases} S\frac{\partial T}{\partial V} - V\frac{\partial P}{\partial V} = 0 \\ S\frac{\partial T}{\partial N} - V\frac{\partial P}{\partial N} = 0 \\ S\frac{\partial T}{\partial \mu} - V\frac{\partial P}{\partial \mu} + N = 0. \end{cases}$$

The area conditions become

$$\begin{cases} \frac{\partial S}{\partial N}\frac{\partial T}{\partial V} - \frac{\partial S}{\partial V}\frac{\partial T}{\partial N} + \frac{\partial P}{\partial N} = 0 \\ \frac{\partial S}{\partial \mu}\frac{\partial T}{\partial V} - \frac{\partial S}{\partial V}\frac{\partial T}{\partial \mu} + \frac{\partial P}{\partial \mu} = 0 \\ \frac{\partial S}{\partial \mu}\frac{\partial T}{\partial N} - \frac{\partial S}{\partial N}\frac{\partial T}{\partial \mu} - 1 = 0. \end{cases}$$

Open problem. Find the general solution.

20) For the case of considering the state variables $x = P$, $y = N$, $z = \mu$, i.e.,

$$s(P, N, \mu)$$
$$= (S(P, N, \mu), T(P, N, \mu), V(P, N, \mu), P, N, \mu),$$

the PDE system (5) becomes

$$\begin{cases} S\frac{\partial T}{\partial P} - V = 0 \\ S\frac{\partial T}{\partial N} = 0 \\ S\frac{\partial T}{\partial \mu} + N = 0, \end{cases}$$

and the PDE system (6) rewrites

$$\begin{cases} \frac{\partial S}{\partial N}\frac{\partial T}{\partial P} - \frac{\partial V}{\partial N} - \frac{\partial S}{\partial P}\frac{\partial T}{\partial N} = 0 \\ \frac{\partial S}{\partial \mu}\frac{\partial T}{\partial P} - \frac{\partial V}{\partial \mu} - \frac{\partial S}{\partial P}\frac{\partial T}{\partial \mu} = 0 \\ \frac{\partial S}{\partial \mu}\frac{\partial T}{\partial N} - \frac{\partial S}{\partial N}\frac{\partial T}{\partial \mu} - 1 = 0. \end{cases}$$

The simplest solution has the form

$$S = -N\left(\frac{\partial T(P,\mu)}{\partial \mu}\right)^{-1},$$
$$T = T(P,\mu),$$
$$V = -N\left(\frac{\partial T(P,\mu)}{\partial \mu}\right)^{-1}\left(\frac{\partial T(P,\mu)}{\partial P}\right),$$

where $T(P,\mu)$ is an arbitrary function.

5 Conclusions

This paper applies our point of view developed in [2]-[11] to a Gibbs-Duhem-Pfaff equation in Thermodynamics, Chemistry etc, enlightening the mathematical theory in [1]. Since in our variant the Gibbs-Duhem-Pfaff equation has 6 variables and it is not completely integrable, the integral submanifolds have at most the dimension 3. These integral submanifolds are described as regular functions of class C^2. The most important cases are those in which the state variables are between *measurable variables* in the set $\{$pressure=P, temperature=T, volume=$V\}$. All the theory can be transferred to the *nonholonomic economic systems* via the original dictionary in [7]-[11].

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