

## On the classification of phase transitions

T. Matolcsi

**Abstract.** A new classification of phase transitions is presented, based on an exact mathematical model of phase, on rigorous definitions and results regarding phase transitions which are classified to be of zeroth, second and first order. Then the relation between the known classifications due to Ehrenfest and Tisza, respectively, becomes clear.

**Mathematics Subject Classification (1991).** 80A97, 80A22.

**Keywords.** Classical thermodynamics, phase transitions.

### 1. Introduction

It is well known that there are two classifications of phase transitions in thermodynamics, due to Ehrenfest and Tisza, respectively ([1],[2]). They differ significantly: Ehrenfest's classification is "applicable to those transitions in which the discontinuities of the derivatives are simple jumps" and is based on *intensive variables* (the chemical potential and its derivatives as functions of temperature and pressure are considered); Tisza's classification "is applicable to those transitions in which discontinuities are infinite values of the derivatives" and is based on *extensive variables* (stability criteria are examined in terms of extensive variables).

Second order phase transitions of Ehrenfest type are rarely observed in nature; on the contrary,  $\lambda$ -transitions which correspond to Tisza's classification, are common phenomena. Since such transitions are related to the lack of stability conditions, it is frequently stated that phase transitions, in general, are connected with the loss of stability:

"The criteria of stability must be satisfied by the fundamental equation of any system that is to remain homogeneous and stable. If the stability criteria are not satisfied, the system breaks into two or more portions. This separation is called phase transition." "...the equation of state does not everywhere satisfy the criteria of intrinsic stability... A phase transition consequently must occur in this substance..." ([2], pp. 146,148).

"States with indefinite forms cannot exist in nature and they break up into one

or more phases.” ([1], p.224)

However, it is well known that liquid water under everyday circumstances (normal temperature and pressure) is stable, nevertheless it evaporates. Moreover, the well known discussion of Van der Waals gases shows without doubt that the boiling of liquids begins in a region of intrinsic stability ([2]). Stability and first order phase transitions are not in the relation claimed by the cited statements.

This is well reflected in the fact that first order phase transitions do not appear in Tisza’s classification.

Examining the two classifications we find that

– *first order phase transitions are well described in Ehrenfest’s classification and are not present in Tisza’s classification,*

– *most of the second order phase transitions –  $\lambda$ -transitions – are well described in Tisza’s classification and are not described in Ehrenfest’s classification.*

Now two questions arise:

1. What is the exact relation between the two classifications?
2. Is there a classification which well describes both first order and second order phase transitions?

This article is devoted to answer these questions.

Before going into detail, let me mention that the name phase transition in this respect is somewhat misleading because transition in everyday language means a process. Thus phase transition should mean the process of phase change (e.g. the one that initially there are given hundred grams of ice under certain circumstances, the ice begins to melt and after  $t$  minutes the mass of ice is  $m(t)$  and the mass of water is  $100g - m(t)$ ). There are papers dealing with phase transitions indeed i.e. describing some aspects of the dynamics of phase change ([3],[4],[5],[6]) but in the mentioned classifications no such a transition is treated; the Clausius-Clapeyron equation, the classifications of Ehrenfest and Tisza characterize the phase lines and phase surfaces that appear on the well known phase diagrams and which are called sometimes phase boundaries ([7]); however, we shall see that, in general, they are not boundaries in the usual mathematical sense. Since these lines and surfaces mean some connection between different phases, I shall use the name *phase connection* instead of phase transition or phase boundary. In this terminology we can say that a phase transition can occur between two phases being in a phase connection.

Of course, to deal with phase connections, first we must have an exact definition of phases. In general, different phases are considered to be described by different constitutive functions (state functions)([3],[4],[5]). However, the liquid and the gaseous phases intermingle over the critical point (Fig 1); therefore these phases cannot be described consistently by different constitutive functions.

We call attention to that the domain of constitutive functions will play an important role in the precise description and classification of phase connections.

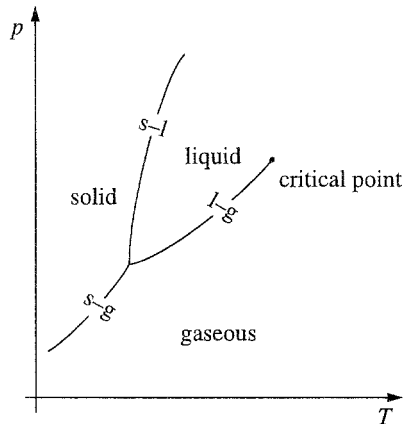


Figure 1.

## 2. Mathematical tools

### 2.1. Differentiation

Let  $\mathbf{V}$  and  $\mathbf{U}$  be finite dimensional vector spaces; if  $f : \mathbf{V} \rightarrow \mathbf{U}$  is differentiable at  $\mathbf{x} \in \mathbf{V}$  then its derivative is a linear map  $f'(\mathbf{x}) : \mathbf{V} \rightarrow \mathbf{U}$ .

In particular, for the derivative of a differentiable function  $f : \mathbb{R}^n \rightarrow \mathbb{R}$ , we have  $f'(x_1, \dots, x_n) = \left( \frac{\partial f(x_1, \dots, x_n)}{\partial x_1}, \dots, \frac{\partial f(x_1, \dots, x_n)}{\partial x_n} \right)$ . Accordingly, the derivative of the joint of  $n$  functions  $(f_1, \dots, f_n) : \mathbb{R}^n \rightarrow \mathbb{R}^n$ ,  $(f'_1, \dots, f'_n)$  is the corresponding Jacobian matrix.

The second derivative of a twice differentiable  $f : \mathbf{V} \rightarrow \mathbf{U}$  at  $\mathbf{x} \in \mathbf{V}$  is a bilinear map  $f''(\mathbf{x}) : \mathbf{V} \times \mathbf{V} \rightarrow \mathbf{U}$ . In the case  $\mathbf{U} = \mathbb{R}$  it makes sense that  $f''(\mathbf{x})$  is negative definite, negative semi-definite, indefinite, etc.

### 2.2. Diagonal spaces

(i) Let  $n > 1$  be a positive integer and put

$$\mathbf{D}_{n-1} := \left\{ (x_1, \dots, x_n) \in \mathbb{R}^n \mid \sum_{i=1}^n x_i = 0 \right\},$$

$$D_{n-1} := \left\{ (c_1, \dots, c_n) \in \mathbb{R}^n \mid \sum_{i=1}^n c_i = 1 \right\}.$$

$\mathbf{D}_{n-1}$  is an  $n-1$  dimensional linear subspace of  $\mathbb{R}^n$  and  $D_{n-1}$  is an affine space over  $\mathbf{D}_{n-1}$  i.e. the difference of two elements of  $D_{n-1}$  is in  $\mathbf{D}_{n-1}$ .

Choosing a  $k = 1, \dots, n$  and omitting the  $k$ -th coordinates, we can represent the elements of  $\mathbf{D}_{n-1}$  by the elements of  $\mathbb{R}^{n-1}$ ; in other words, we can establish a linear bijection ("coordinatization")  $\mathbf{R}_k : \mathbf{D}_{n-1} \rightarrow \mathbb{R}^{n-1}$ . This does not mean, however, that  $\mathbf{D}_{n-1}$  and  $\mathbb{R}^{n-1}$  are identical.

Similarly, omitting the  $k$ -th coordinates, we can represent the elements of  $D_{n-1}$  by the elements of  $\mathbb{R}^{n-1}$ ; in other words, we can establish an affine bijection ("coordinatization")  $R_k : D_{n-1} \rightarrow \mathbb{R}^{n-1}$ .

All  $R_k$ -s, though being different, play equal role. For the sake of definiteness, in the following we consider  $R_n$ . We have that

$$\mathbf{R}_n^{-1}(x_1, \dots, x_{n-1}) = \left( x_1, \dots, x_{n-1}, -\sum_{i=1}^{n-1} x_i \right),$$

$$R_n^{-1}(c_1, \dots, c_{n-1}) = \left( c_1, \dots, c_{n-1}, 1 - \sum_{i=1}^{n-1} c_i \right).$$

(ii) A linear map  $P : \mathbf{D}_{n-1} \rightarrow \mathbb{R}$  can be given by an element  $(p_1, \dots, p_n)$  of  $\mathbb{R}^n$  in such a way that

$$P(x_1, \dots, x_n) = \sum_{i=1}^n p_i x_i.$$

We shall write that  $P = ((p_1, \dots, p_n))$ . It is a simple fact that  $((q_1, \dots, q_n)) = ((p_1, \dots, p_n))$  if and only if there is a number  $c$  such that  $q_i = p_i + c$  for all  $i = 1, \dots, n$ . Using the coordinatization  $\mathbf{R}_n$  we represent this linear map by the element  $(p_i - p_n \mid i = 1, \dots, n - 1)$  of  $\mathbb{R}^{n-1}$ .

(iii) The differentiability of a function  $f : D_{n-1} \rightarrow \mathbb{R}$  at  $(c_1, \dots, c_n)$  is defined by the usual formula; its derivative is a linear map  $f'(c_1, \dots, c_n) : \mathbf{D}_{n-1} \rightarrow \mathbb{R}$

Note the important fact that the derivative of  $f$  is not the collection of partial derivatives (partial derivatives of  $f$  make no sense: the coordinates in  $D_{n-1}$  cannot vary independently from each other). However, using the coordinatization  $R_n$ , the collection of the  $n - 1$  partial derivatives of  $f \circ R_n^{-1}$  will represent  $f'$ : if  $f'(c_1, \dots, c_n) = ((d_1, \dots, d_n))$  then

$$\frac{\partial f(R_n^{-1}(c_1, \dots, c_{n-1}))}{\partial c_k} = d_k - d_n \quad (k = 1, \dots, n - 1).$$

### 2.3. Curves, surfaces

(i) Let  $\mathbf{V}$  be a finite dimensional vector space,  $n := \dim \mathbf{V}$ . Let  $k$  be a positive integer,  $k < n$ .

A subset  $S$  of  $\mathbf{V}$  is a  $k$  dimensional surface if every point of  $S$  has a neighbourhood  $U$  for which there is a function  $r : \mathbb{R}^k \rightarrow \mathbf{V}$ , called a parametrization of  $S$  in  $U$ , such that

- the domain of  $r$  is a connected open subset,
- the range of  $r$  equals  $S \cap U$ ,
- $r$  is continuously differentiable,
- $r'$  is everywhere injective,
- $r$  is injective,
- $r^{-1}$  is continuous.

The one dimensional surfaces and the  $n - 1$  dimensional surfaces are called *curves* and *hypersurfaces*, respectively.

Note that hypersurfaces in a two dimensional vector space are curves.

(ii) It follows from the implicit function theorem that if  $Z : \mathbf{V} \rightarrow \mathbb{R}^{n-k}$  is continuously differentiable, 0 is in the range of  $Z$  and  $Z'(x)$  is surjective for all  $S := \{x \in \mathbf{V} \mid Z(x) = 0\}$  then  $S$  is a  $k$ -dimensional surface.

(iii) Every point of a hypersurface  $S \subset \mathbf{V}$  has a connected neighbourhood  $N$  such that  $N \setminus S$  is the disjoint union of two connected open subsets.

Indeed, choose an arbitrary point  $x_0$  of  $S$  and a parametrization  $r$  of  $S$  in a neighbourhood of  $x_0$ . Without loss of generality we can suppose that  $r(0) = x_0$ . Take a vector  $v \in \mathbf{V}$ , linearly independent of the range of  $r'(0)$  (which is an  $n - 1$  dimensional linear subspace). The function  $\varphi : \mathbb{R}^{n-1} \times \mathbb{R} \rightarrow \mathbf{V}$ ,  $(t, s) \mapsto r(t) + sv$  is continuously differentiable and its derivative at  $(0, 0)$  equals  $(r'(0), v)$ . Then we infer from the inverse function theorem that there are a connected open subset  $J \subset \mathbb{R}^{n-1}$  and an open interval  $I$  such that the restriction of  $\varphi$  onto  $J \times I$  is injective and its inverse is continuously differentiable, too (which implies that it maps connected open subsets into connected open subsets).

Putting  $N := \varphi[J \times I]$  we have that  $S \cap N = \varphi[J \times \{0\}]$  and  $N \setminus S$  is the disjoint union of the connected open subsets  $\varphi[J \times \{s \in I \mid s < 0\}]$  and  $\varphi[J \times \{s \in I \mid s > 0\}]$ .

(iv) We say that a hypersurface  $S \subset \mathbf{V}$  *separates* the open subsets  $H_1$  and  $H_2$  if

- $H_1$  and  $H_2$  are disjoint,
- every point of  $S$  has a neighbourhood  $N$  such that  $N \setminus S = N_1 \cup N_2$  where  $N_1$  and  $N_2$  are disjoint connected open subsets,  $N_1 \subset H_1$  and  $N_2 \subset H_2$ .

If  $S$  separates  $H_1$  and  $H_2$  then  $S \subset \overline{H_1} \cap \overline{H_2}$

## 2.4. Sidewise derivatives

(i) Suppose the hypersurface  $S \subset \mathbf{V}$  separates the connected open subsets  $H_1$  and  $H_2$  and  $f$  is a (vector valued) function defined on  $H_1 \cup C \cup H_2$ . We say that  $f$  is continuously differentiable on  $S$  from the side of  $H_l$  ( $l = 1, 2$ ) if every point of  $S$  has a neighbourhood  $N$  with the property stated in 2.3.(iv) such that there is a continuously differentiable functions  $f_l$  defined on  $N$  and  $f_l(x) = f(x)$  for  $x \in S \cup N_l$ .

If  $f$  is continuously differentiable from the side of  $H_l$  then the quantity  $f'_l(x)$  ( $l = 1, 2$ ) is called the corresponding *sidewise derivative* of  $f$  at  $x \in S$ .

(ii) Use the previous notations and suppose  $f$  is continuously differentiable on  $S$  from both sides. Then  $f$  is continuously differentiable (in the usual sense) at  $x \in S$  if  $f'_1(x) = f'_2(x)$  and is not differentiable at  $x \in S$  if  $f'_1(x) \neq f'_2(x)$ .

## 2.5. Physical quantities

(i) We shall distinguish between functions and their values: italic letters denote values, functions are denoted by another type of letters (boldface etc.). Thus  $e, v, T, p$  stand for values of specific energy, specific volume, temperature and pressure, respectively, and  $\mathbf{e}, \mathbf{v}, \mathbf{T}, \mathbf{p}$  indicate specific energy, specific volume, temperature and pressure as functions of  $e$  and  $v$ .

(ii) The set of possible values of specific internal energy and specific volume – the  $(e - v)$ -plane – is quite different from the set of possible temperature and pressure values – the  $(T - p)$ -plane. Nevertheless, both are frequently considered to be  $\mathbb{R}^2$ . For a clear distinction, we shall take into account the "physical dimension" of the quantities which will be measured in SI units:

- time:  $s$  (second)
- distance:  $m$  (meter)
- volume:  $m^3$
- mass:  $kg$  (kilogram)
- energy:  $J$  (Joule =  $kgm^2/s^2$ )
- pressure:  $Pa$  (Pascal =  $kg/ms^2$ )
- temperature:  $K$  (Kelvin)

Then, for instance, the values of temperature are positive multiples of  $K$  i.e. they are elements of

$$(K)^+ := \{\alpha K \mid \alpha \in \mathbb{R}, \alpha > 0\}.$$

Similarly, we shall use the notations

$$(kg)_0^+ := \{\alpha kg \mid \alpha \in \mathbb{R}, \alpha \geq 0\}, \quad (J/kg) := \{\alpha(J/kg) \mid \alpha \in \mathbb{R}\}$$

etc. The exact mathematical meaning of the symbols  $J/kg, ms^2$  etc. can be found in [8] or [9].

In these notations the  $(e - v)$ -plane is  $(J/kg) \times (m^3/kg)$  and the  $(T - p)$ -plane is  $(K) \times (Pa)$ , and their positive quadrant contains the physically meaningful values.

The vector space structure and the topological properties of the real line can be transferred trivially to the above objects. Thus we can speak of continuity and differentiability of functions defined or having values in them. In particular, e.g. we can speak of a curve in  $(J/kg)^+ \times (m^3/kg)^+$  and in  $(K)^+ \times (Pa)^+$ .

### 3. Substances, phases

**Definition 1.** A *single-component substance* is a triplet  $(D, \mathbf{s}, R)$  where

(i)  $D$ , called the *constitutive domain*, is a non-void subset of  $(J/kg)^+ \times (m^3/kg)^+$ ; the first and second variables in  $D$  (usually denoted by  $e$  and  $v$ , respectively), are the *specific internal energy* and the *specific volume*, respectively; the elements of  $D$  are called *states* of the substance,

(ii)  $\mathbf{s} : D \rightarrow (J/kgK)$ , the *specific entropy*, is continuously differentiable and its partial derivatives are everywhere positive,

(iii)  $R$ , the *regular constitutive domain*, is an open subset, consisting of the elements  $(e, v) \in D$  such that  $\mathbf{s}$  is twice continuously differentiable at  $(e, v)$  and  $\mathbf{s}''(e, v)$  is negative definite.

**Remarks 1.** (i) The *temperature*  $\mathbf{T} : D \rightarrow (K)^+$  and the *pressure*  $\mathbf{p} : D \rightarrow (Pa)^+$  of the substance, defined by

$$\frac{1}{\mathbf{T}} = \frac{\partial \mathbf{s}}{\partial e}, \quad \frac{\mathbf{p}}{\mathbf{T}} = \frac{\partial \mathbf{s}}{\partial v},$$

as well as the *chemical potential*

$$\mu := \mathbf{e} + \mathbf{p}v - \mathbf{T}\mathbf{s} : D \rightarrow (J/kg)$$

are continuous on  $D$  and continuously differentiable on  $R$ .

(ii) The negative definiteness of  $\mathbf{s}''(e, v)$  is equivalent to the inequalities

$$\frac{\partial \mathbf{T}(e, v)}{\partial e} > 0, \quad \frac{\partial \mathbf{T}(e, v)}{\partial e} \frac{\partial \mathbf{p}(e, v)}{\partial v} - \frac{\partial \mathbf{T}(e, v)}{\partial v} \frac{\partial \mathbf{p}(e, v)}{\partial e} < 0.$$

(iii) The Jacobian determinant of the joint function  $(\mathbf{T}, \mathbf{p})$  is the expression on the left hand side of the second inequality above. As a consequence of the well known inverse function theorem,  $(\mathbf{T}, \mathbf{p})$  is a local diffeomorphism in  $R$ , i.e. every point in  $R$  has a neighbourhood in which  $(\mathbf{T}, \mathbf{p})$  is injective and its inverse is continuously differentiable as well. In other words, at least locally, the specific internal energy and the specific volume in  $R$  can be given as a continuously differentiable function of temperature and pressure. Moreover, if  $H$  is an open subset of  $R$  then  $(\mathbf{T}, \mathbf{p})[H]$  is an open subset in  $(K)^+ \times (Pa)^+$ .

It is worth mentioning that  $(\mathbf{T}, \mathbf{p})$  is injective if and only if  $(1/\mathbf{T}, \mathbf{p}/\mathbf{T}) = \mathbf{s}'$  is injective.

(iv) If  $(e, v) \in D \setminus R$  then either  $\mathbf{s}'$  is not continuously differentiable at  $(e, v)$  or  $\mathbf{s}''(e, v)$  is not negative definite; equivalently,  $(\mathbf{T}, \mathbf{p})$  is not continuously differentiable at  $(e, v)$  or at least one of the inequalities in (ii) is not satisfied.

Now we focus our attention on phases. Recall that different phases need not be disjoint: the liquid phase and the gaseous phase of a substance intermingle over

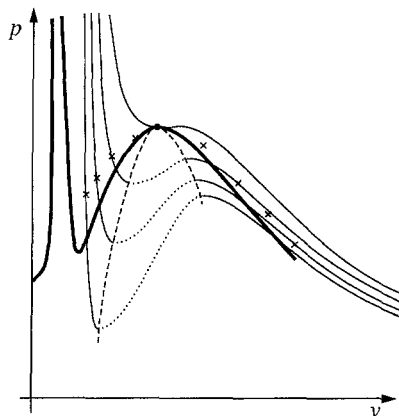


Figure 2.

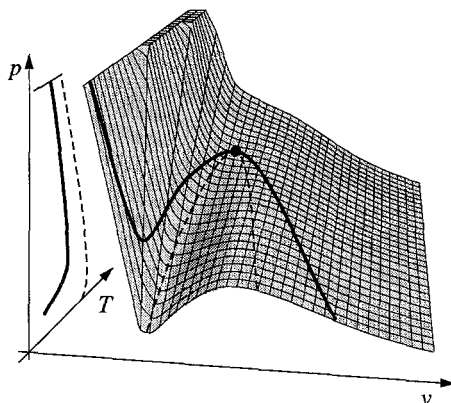


Figure 3.

the critical point which can be seen in the usual phase diagram in Fig.1. What makes then distinction between the two phases? For getting a convenient answer, let us recall some well known facts.

Fig.2 shows the well known picture of isotherms in the  $(p - v)$ -plane of Van der Waals gases. The dashed lines ("spinodal lines") represent the edge of the "physical region" (i.e. the part corresponding to the regular constitutive domain), the dotted lines mark the "unphysical part" of isotherms; the continuous fat lines ("binodal lines") represent the phase equilibrium states. The meaning of the star lines will be explained later.

We know the picture of isobars in the  $(T - v)$ -plane, too ([10]). Then we can reconstruct a three dimensional phase diagram in the  $(p - T - v)$ -space (Fig.3). The picture in the  $(p - e - v)$ -space will be similar, perhaps only distorted a little



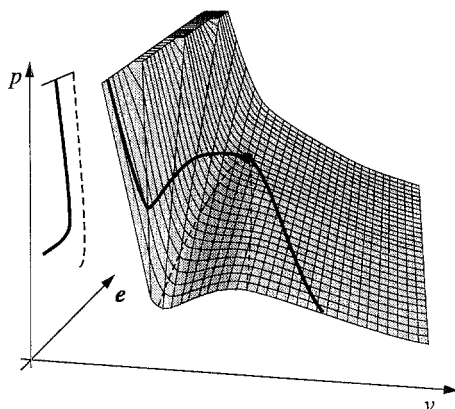


Figure 4.

(for a Van der Waals gas in the simplest case  $\mathbf{T}(e, v) = \gamma(e + a/v)$  where  $\gamma$  and  $a$  are positive constants) (Fig.4).

A profound study of these diagrams leads us to the following definition.

**Definition 2.** A *phase* of a single-component substance  $(D, \mathbf{s}, R)$  is a connected open subset  $F$  of  $R$  such that

- (i)  $\mathbf{s}'$  is injective on  $F$ ,
- (ii)  $F$  is maximal with this property (i.e. if  $N$  is a connected open subset of  $R$  containing  $F$  and  $\mathbf{s}'$  is injective on  $N$  then  $N = F$ ).

**Proposition 1.** *Every point of  $R$  is in a phase.*

*Proof.* Every point  $(e, v)$  of  $R$  has a neighbourhood in which  $\mathbf{s}'$  is injective. Let  $\mathcal{F}$  be the family of the connected open subsets, containing  $(e, v)$ , that  $\mathbf{s}'$  is injective on.  $\mathcal{F}$  is ordered by the inclusion. Take a chain in  $\mathcal{F}$ ; the union of the subsets in the chain is in  $\mathcal{F}$  and is an upper bound of the chain. Thus Zorn's lemma yields that  $\mathcal{F}$  has a maximal element; it is evidently a phase containing  $(e, v)$ .

**Remarks 2.** (i) The definition admits, indeed, that a point belong to more than one phase: different phases need not be disjoint.

(ii) The star lines in Fig.2 indicate the borders of the liquid and gaseous phases in the  $(p - v)$ -plane. The border line on the left hand side of the critical point is constructed as follows: draw a horizontal line across the local maximum of an isotherm (under the critical value) and take the point where this horizontal line meets the isotherm in question. A similar construction – with minimum instead of maximum – yields the border line on the right hand side of the critical point.

The gaseous phase is the region over the left border line and right spinodal line; the liquid phase is the region over the left spinodal line and the right border

line.

(iii) Recall that the injectivity of  $\mathbf{s}'$  is equivalent to the injectivity of  $(\mathbf{T}, \mathbf{p})$ . If  $F$  is a phase then

$$\phi := (\mathbf{T}, \mathbf{p})[F]$$

is a connected open subset of  $(K)^+ \times (Pa)^+$ . As usual, let a vertical bar denote the restriction of functions, and introduce the notations

$$(e_F, v_F) := ((\mathbf{T}, \mathbf{p})|_F)^{-1} : \phi \rightarrow F, \quad \mu_F := \mu \circ (e_F, v_F) : \phi \rightarrow (J/kg).$$

In other words, specific internal energy and specific volume – consequently the chemical potential, too – in a phase are given as continuously differentiable functions of temperature and pressure; note that  $\mu_F(T, p) = \mu((e_F(T, p), v_F(T, p)))$  for all  $(T, p) \in \phi$ .

The Gibbs-Duhem relations read in these notations as follows:

$$\frac{\partial \mu_F}{\partial T} \circ (\mathbf{T}, \mathbf{p}) = -\mathbf{s}|_F, \quad \frac{\partial \mu_F}{\partial p} \circ (\mathbf{T}, \mathbf{p}) = \mathbf{v}|_F.$$

(iv) Regarding phase connections, two phases  $F_1$  and  $F_2$  will be involved. Then we shall use the notations for  $l = 1, 2$ :

$$\begin{aligned} \phi_l &:= (\mathbf{T}, \mathbf{p})[F_l], & (\mathbf{T}_l, \mathbf{p}_l) &:= (\mathbf{T}, \mathbf{p})|_{F_l}, \\ (e_l, v_l) &:= (\mathbf{T}_l, \mathbf{p}_l)^{-1}, & \mu_l &:= \mu \circ (e_l, v_l). \end{aligned}$$

#### 4. Zeroth-order phase connections

Phase diagrams, such as the one in Fig.1, are usually given in the  $(T - p)$ -plane. Consequently, usual phase lines are subsets of the  $(T - p)$ -plane.

The intensive parameters characterize a phase completely; however, they do not characterize necessarily two phases:  $(\mathbf{T}, \mathbf{p})$  is injective on a phase but is not necessarily injective on the union of two phases.

Therefore it seems, it is better to describe phase connections in the  $(e - v)$ -plane, all the more because phases are defined to be subsets of that plane.

The liquid phase and the gaseous phase are not disjoint; thus it is possible that a process starts from a definitely liquid state and then through continuous changes it arrives at a definitely gaseous state. Of course, such a process is a phase transition which is characterized by the facts that

– the extensive quantities (specific internal energy and specific volume) and the intensive quantities (given by the constitutive functions) and their derivatives change continuously.

A similar phase transition can occur if disjoint phases have a common boundary in the regular constitutive domain.

Such processes can be called a zeroth-order phase transitions.

**Definition 3.** The *zeroth-order phase connection* of the phases  $F_1$  and  $F_2$  of a single-component substance is  $R \cap \overline{F_1} \cap \overline{F_2}$ ; if this set is not empty then the two phases are said to be *in zeroth-order connection*.

**Remarks 3.** (i) With the usual notation for the boundary of sets ( $\partial F := \overline{F} \setminus F$ , so  $\overline{F} = F \cup \partial F$ ) and taking into account that the phases are subsets of  $R$ , we can transform the zeroth order phase connection of  $F_1$  and  $F_2$  in the form

$$(F_1 \cap F_2) \cup (F_1 \cap \partial F_2) \cup (\partial F_1 \cap F_1) \cup (\partial F_1 \cap \partial F_2 \cap R).$$

(ii) If  $F_1$  and  $F_2$  are not disjoint then  $F_1 \cap F_2$  is a non-void open subset in the zeroth-order phase connection and  $F_1 \setminus \overline{F_2}$  is the largest open subset in  $F_1$ , disjoint from  $F_2$ ; this is the part of  $F_1$  which is "definitely"  $F_1$  in contrast to  $F_2$ .

## 5. Second-order phase connections

In second order phase transitions

– the extensive quantities as well as the intensive quantities change continuously, but some of their derivatives change discontinuously.

This indicates that in such a process the state leaves a phase and enters another one through a common boundary point which does not belong to the regular constitutive domain.

**Definition 4.** The *second-order phase connection* of the phases  $F_1$  and  $F_2$  of a single-component substance  $(D, \mathbf{s}, R)$  is  $(D \setminus R) \cap \overline{F_1} \cap \overline{F_2}$ ; if this set is not empty then the two phases are said to be *in a second-order phase connection*.

**Remark 4.** Since the phases are disjoint from  $D \setminus R$ , the second-order phase connection of  $F_1$  and  $F_2$  can be transformed into the form

$$\partial F_1 \cap \partial F_2 \cap (D \setminus R);$$

thus only boundary points of the phases are contained in the second-order phase connection.

In Tisza's classification the differentiability is not questioned, only the lack of intrinsic stability is required.

**Definition 5.** A point  $(e, v)$  of a second-order phase connection is called of *Tisza type* if  $\mathbf{s}'$  is continuously differentiable at  $(e, v)$  but  $\mathbf{s}''(e, v)$  is not negative definite.

A subset of the second-order phase connection is of Tisza type if all of its points are of Tisza type.

**Remark 5.** Because of the continuous differentiability, the second derivative of  $s$  at a Tisza type point is negative semi-definite.

Ehrenfest’s classification involves sidewise derivatives; therefore, to define Ehrenfest type second-order phase connection, we need the following notion.

**Definition 6.** A subset  $C$  of the second order phase connection between the phases  $F_1$  and  $F_2$  is called a *regular part* if

- (i)  $C$  is a curve which separates  $F_1 \setminus \overline{F_2}$  and  $F_2 \setminus \overline{F_1}$ ,
- (ii)  $s'$  is injective on an open subset  $G$  containing  $C$ ,
- (iii)  $s'$  is continuously differentiable on  $C$  from both sides.

**Remarks 6.** (i) Put

$$H_1 := F_1 \setminus \overline{F_2}, \quad H_2 := F_2 \setminus \overline{F_1}.$$

According to the definition of a phase,  $s'$  is continuously differentiable on  $H_1$  and  $H_2$ . Moreover, the sidewise continuous differentiability on  $C$  means that every point of  $C$  has a neighbourhood  $N$  (satisfying the properties listed in 2.3.(iv)) on which continuously differentiable functions  $s'_1$ , and  $s'_2$  can be defined such that  $s'_1(e, v) = s'(e, v)$  for  $(e, v) \in N_1$  and  $s'_2(e, v) = s'(e, v)$  for  $(e, v) \in N_2$ . (The functions  $s'_1$  and  $s'_2$  have no physical meaning on  $N_2$  and  $N_1$ , respectively, they serve only for the convenient mathematical expression of continuous sidewise differentiability on  $C$ .)

(ii)  $C$  is disjoint from  $R$  and is contained in  $\overline{R}$ . Because of the continuity, the sidewise derivatives of  $s'$  at every point of  $C$  are negative definite or negative semi-definite.

(iii)  $s'$  and  $(\mathbf{T}, \mathbf{p})$  determine each other uniquely. Thus  $(\mathbf{T}, \mathbf{p})$  is continuously differentiable on  $C$  from both sides.

(iv) Specific internal energy and specific volume can be given as a function of temperature and pressure in a neighbourhood of a regular part of a second-order phase connection. More precisely, put

$$\Gamma := (\mathbf{T}, \mathbf{p})[C] \quad \Omega := (\mathbf{T}, \mathbf{p})[G],$$

and

$$\Omega_1 := (\mathbf{T}, \mathbf{p})[G \cap H_1] \quad \Omega_2 := (\mathbf{T}, \mathbf{p})[G \cap H_2].$$

For  $l = 1, 2$ ,  $\Omega_l$  is an open subset in  $\phi_l$ , and  $(e, v) := ((\mathbf{T}, \mathbf{p})|_G)^{-1}$  is a function defined on  $\Omega$  for which  $(e, v)(T, p) = (e_l, v_l)(T, p)$  holds if  $(T, p) \in \Omega_l$  ( $l = 1, 2$ ).

**Definition 7.** A regular part  $C$  of a second-order phase connection is called of *Ehrenfest type* if at every point of  $C$  both sidewise derivatives of  $\mathbf{s}'$  are negative definite.

The next proposition shows that our definition of Ehrenfest type second-order phase connection coincides with the original one based on intensive variables.

**Proposition 2.** *Suppose  $C$  is an Ehrenfest type regular part of a second-order phase connection and use the previous notations. Then*

- (i)  $\Gamma$  is a curve,
- (ii)  $(e, v)$  and consequently  $\mu := \mu \circ (e, v)$  are continuously differentiable on  $\Gamma$  from both sides,
- (iii)  $\Gamma$  is described by the Ehrenfest differential equation (detailed below).

*Proof.* Let  $(T_0, p_0)$  be an arbitrary point of  $\Gamma$ . Then there is a unique  $(e_0, v_0)$  in  $C$  such that  $T_0 = \mathbf{T}(e_0, v_0)$  and  $p_0 = \mathbf{p}(e_0, v_0)$ . Let  $(\mathbf{T}_1, \mathbf{p}_1)$  and  $(\mathbf{T}_2, \mathbf{p}_2)$  be the continuously differentiable functions defined on a neighbourhood  $N \subset G$  of  $(e_0, v_0)$  that correspond to the sidewise continuous differentiability of  $(\mathbf{T}, \mathbf{p})$  on  $C$ . Their derivatives on  $C$  are invertible because they satisfy the second inequality in Remark 1 (i). Consequently, if  $r$  is a parametrization of  $B$  in  $N$  then  $(\mathbf{T}_1, \mathbf{p}_1) \circ r = (\mathbf{T}_2, \mathbf{p}_2) \circ r$  is a parametrization of  $\Gamma$  in  $(\mathbf{T}, \mathbf{p})[N]$ , thus  $\Gamma$  is a curve.

From the continuity of  $(\mathbf{T}, \mathbf{p})$  and from the fact that  $C$  separates  $G \cap H_1$  and  $G \cap H_2$ , we infer that  $\Gamma$  separates  $\Omega_1$  and  $\Omega_2$ ; thus the continuous sidewise differentiability of  $(e, v)$  on  $\Gamma$  is meaningful.

It follows from the inverse function theorem that  $(\mathbf{T}_l, \mathbf{p}_l)$  ( $l = 1, 2$ ) are injective on an open subset contained in  $N$  and their inverses are continuously differentiable. We can suppose without loss of generality that this open set equals  $N$ . Then  $(\mathbf{T}_l, \mathbf{p}_l)^{-1}$  are the functions that define the sidewise derivatives of  $(e, v)$  on  $\Gamma$ .

The sidewise derivatives of  $\mathbf{s}'$  on  $C$  are negative definite; consequently, the two sidewise derivatives of  $(\mathbf{T}, \mathbf{p})$  at every point of  $C$  are different (if they were equal at a point then that point would be in the regular domain, see 2.4.(ii)). Hence the sidewise derivatives of  $(e, v)$  on  $\Gamma$  are different as well: with the notation

$$(\kappa_l(T, p), \alpha_l(T, p)) := e'_l(T, p)$$

for all  $(T, p) \in \Gamma$  we have

$$\kappa_2(t, p) - \kappa_1(T, p) \neq 0 \quad \text{or} \quad \alpha_2(t, p) - \alpha_1(T, p) \neq 0.$$

Let  $(T_0, p_0)$  be an element of  $\Gamma$  and suppose  $\kappa_2(T_0, p_0) - \kappa_1(T_0, p_0) \neq 0$ . Then by the continuity,  $(T_0, p_0)$  has a neighbourhood  $\Delta \subset \Omega$  such that for all  $(T, p) \in \Gamma \cap \Delta$  the non-equality holds.

Then from the formula

$$\Gamma \cap \Delta = \{(T, p) \in \Delta \mid e_2(T, p) - e_1(T, p) = 0, v_2(T, p) - v_1(T, p) = 0\}$$

and from the implicit function theorem we conclude that  $\Gamma \cap \Delta$  is the graph of a continuously differentiable function  $(K)^+ \mapsto (Pa)^+$  which is the solution of the differential equation

$$\frac{dp}{dT} = \frac{\alpha_2(T, p) - \alpha_1(T, p)}{\kappa_2(T, p) - \kappa_1(T, p)}, \quad p(T_0) = p_0.$$

Of course, if  $\alpha_2(T_0, p_0) - \alpha_1(T_0, p_0) \neq 0$ , we have that  $\Gamma$  in a neighbourhood of  $(T_0, p_0)$  is the graph of a continuously differentiable function  $(Pa)^+ \mapsto (K)^+$  which is the solution of the differential equation

$$\frac{dT}{dp} = \frac{\kappa_2(T, p) - \kappa_1(T, p)}{\alpha_2(T, p) - \alpha_1(T, p)}, \quad T(p_0) = T_0.$$

**Remark 7.** (i) The previous definitions and result exhibit clearly the relation between Tisza's and Ehrenfest's ideas regarding second-order phase connections.

(ii) There are subsets of second-order phase connections which are neither of Tisza type or of Ehrenfest type. It seems, the most important "intermediate" type is the following:  $C$  is a regular part of a second-order phase connection and at every point of  $C$  one of the sidewise derivatives of  $s'$  is negative semi-definite, the other is negative definite. (If both sidewise derivatives are negative definite then  $C$  is of Ehrenfest type; if both are negative semi-definite then  $C$  is of Tisza type.)

The  $\lambda$ -transition of the quartz crystal is of this intermediate type: the heat capacity tends to infinity from one side and tends to a finite value from the other side ([2]).

## 6. First-order phase connections

In a first-order phase transition (e.g. in boiling) the process starts from a definitely liquid state and then abruptly it arrives at a definitely gaseous state. Such a phase transition has the characteristic feature that

– the extensive quantities change discontinuously whereas the intensive ones change continuously.

Fig.1 shows the projection of the surface in Fig.3 onto the  $(T - p)$ -plane. Fig.5 is the projection of the surface in Fig.4 onto the  $(e - v)$ -plane; the projection of the surface in Fig.3 onto the  $(T - v)$ -plane gives a similar picture. Examining the lines of first order phase equilibrium (fat continuous lines), we observe that

(i) one phase line in the  $(T - p)$ -plane corresponds to two phase lines in the  $(e - v)$ -plane (which expresses the fact that specific internal energy and specific volume are not continuous in a first-order phase transition whereas temperature and pressure are continuous),

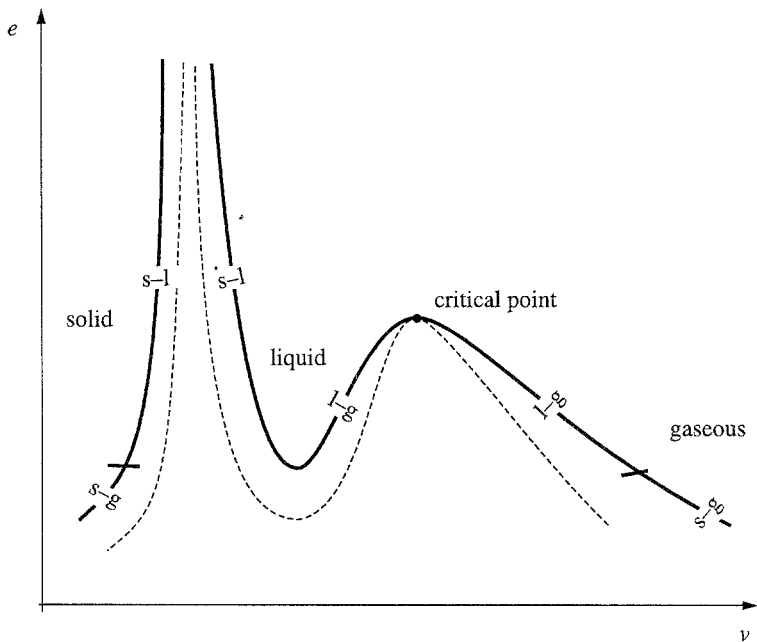


Figure 5.

(ii) the phase lines in the  $(e - v)$ -plane lie in the "physical region" (regular constitutive domain), more closely they lie in the phases and are disjoint from the intersection (the zeroth-order phase connection) of the phases,

(iii) the two phase lines in the  $(e - v)$ -plane are characterized by the property that the intensive variables take equal values on corresponding points.

**Definition 8.** Let  $F_1$  and  $F_2$  be phases of a single-component substance  $(D, s, R)$ ,

$$C_1 := \{(e_1, v_1) \in F_1 \setminus \overline{F_2} \mid \text{there is a } (e_2, v_2) \in F_2 \setminus \overline{F_1}, \\ (\mathbf{T}, \mathbf{p}, \mu)(e_1, v_1) = (\mathbf{T}, \mathbf{p}, \mu)(e_2, v_2)\},$$

$$C_2 := \{(e_2, v_2) \in F_2 \setminus \overline{F_1} \mid \text{there is a } (e_1, v_1) \in F_1 \setminus \overline{F_2}, \\ (\mathbf{T}, \mathbf{p}, \mu)(e_1, v_1) = (\mathbf{T}, \mathbf{p}, \mu)(e_2, v_2)\};$$

the pair  $(C_1, C_2)$  is the *first-order phase connection* of  $F_1$  and  $F_2$ ; if  $C_1$  and  $C_2$  are not void then the two phases are said to be *in a first-order connection*.

**Remarks 8.** (i)  $(\mathbf{T}, \mathbf{p})$  is injective on both  $C_1$  and  $C_2$ ; thus by the very definition of first-order phase connections, there is a one-to-one correspondence between

the two curves: to each  $(e_1, v_1) \in C_1$  there is a unique  $(e_2, v_2) \in C_2$  such that  $\mathbf{T}(e_1, v_1) = \mathbf{T}(e_2, v_2)$  and  $\mathbf{p}(e_1, v_1) = \mathbf{p}(e_2, v_2)$ .

(ii) The images of  $C_1$  and  $C_2$  by  $(\mathbf{T}, \mathbf{p})$  coincide,

$$\Gamma := (\mathbf{T}, \mathbf{p})[C_1] = (\mathbf{T}, \mathbf{p})[C_2],$$

and  $\mu_1(T, p) = \mu_2(T, p)$  for  $(T, p) \in \Gamma$  (notation: Remark 2(iv)).

**Proposition 3.**

$$\Omega := (\mathbf{T}, \mathbf{p})(F_1 \setminus \overline{F_2}) \cap (\mathbf{T}, \mathbf{p})(F_2 \setminus \overline{F_1})$$

is an open set and

$$\Gamma = \{(T, p) \in \Omega \mid \mu_2(T, p) = \mu_1(T, p)\}.$$

*Proof.*  $(\mathbf{T}, \mathbf{p})$  is injective and continuously differentiable on the phases and this holds for its corresponding inverses as well, thus it maps open subsets of the phases into open subsets, consequently  $\Omega$  is open. The definition of the first-order phase connection makes it evident that  $\mu_1(T, p) \neq \mu_2(T, p)$  if  $(T, p) \in \Omega \setminus \Gamma$ .

**Proposition 4.**  $C_1$  and  $C_2$  are curves in  $F_1 \setminus \overline{F_2}$  and  $F_2 \setminus \overline{F_1}$ , respectively, and  $\Gamma$  is a curve in  $\Omega \subset (K)^+ \times (Pa)^+$  described by the Clausius-Clapeyron differential equation.

*Proof.* If  $(T, p) \in \Gamma$  then  $(e_1(T, p), v_1(T, p))$  and  $(e_2(T, p), v_2(T, p))$ , being in  $C_1$  and  $C_2$ , respectively, are distinct. Furthermore,  $s_1(T, p) - s_2(T, p) = e_1(T, p) - e_2(T, p) + p(v_1(T, p) - v_2(T, p))$ ; so if  $v_1(T, p) - v_2(T, p) = 0$  then  $s_1(T, p) - s_2(T, p) \neq 0$ . Consequently, the Gibbs-Duhem relations imply that the derivative of the continuously differentiable function  $\mu_1 - \mu_2$  is not zero on  $\Gamma$ . If  $(T_0, p_0) \in \Gamma$  and  $v_1(T_0, p_0) - v_2(T_0, p_0) \neq 0$  then (because of the continuity of the functions)  $(T_0, p_0)$  has a neighbourhood  $\Delta$  such that  $v_1(T, p) - v_2(T, p) \neq 0$  for all  $(T, p) \in \Gamma \cap \Delta$ . Then from the implicit function theorem we conclude that  $\Gamma \cap \Delta$  is the graph of a continuously differentiable function  $(K)^+ \rightarrow (Pa)$  which is the solution of the differential equation

$$\frac{dp}{dT} = \frac{s_1(T, p) - s_2(T, p)}{v_1(T, p) - v_2(T, p)}, \quad p(T_0) = p_0.$$

If  $v_1(T_0, p_0) - v_2(T_0, p_0) = 0$  then  $s_1(T_0, p_0) - s_2(T_0, p_0) \neq 0$ , and we have that  $\Gamma$  in a neighbourhood of  $(T_0, p_0)$  is the graph of a continuously differentiable function  $(Pa)^+ \rightarrow (K)^+$  which is the solution of the differential equation

$$\frac{dT}{dp} = \frac{v_2(T, p) - v_1(T, p)}{s_2(T, p) - s_1(T, p)}, \quad T(p_0) = T_0.$$



Finally, it is evident now that  $C_1$  and  $C_2$  – images of the curve  $\Gamma$  by the continuously differentiable injective functions  $(\mathbf{T}_1, \mathbf{p}_1)^{-1}$  and  $(\mathbf{T}_2, \mathbf{p}_2)^{-1}$  whose derivatives are everywhere invertible – are curves.

**Definition 9.** Let  $F_1$  and  $F_2$  be two phases with first-order phase connection  $(C_1, C_2)$ . The elements of  $(D \setminus R) \cap \overline{C_1} \cap \overline{C_2}$  are called the *critical points* of the phases.

**Proposition 5.** *The critical points of two phases are in the second-order phase connection of the phases.*

*Proof.* It is evident that the critical points are in  $D \cap \overline{F_1} \setminus \overline{F_2} \cap \overline{F_2} \setminus \overline{F_1}$ , so we have to show only that they are not in the regular constitutive domain. Let  $(e_c, v_c)$  be a critical point and suppose it is in  $R$ . Then it has a neighbourhood in which  $(\mathbf{T}, \mathbf{p})$  is a diffeomorphism. Consequently,  $(T_c, p_c) := (\mathbf{T}(e_c, v_c), \mathbf{p}(e_c, v_c))$  is in the closure of  $\Gamma$ . If  $U$  is an arbitrary neighbourhood of  $(e_c, v_c)$  then  $(\mathbf{T}, \mathbf{p})[U]$  is a neighbourhood of  $(T_c, p_c)$ , thus  $\Gamma \cap (\mathbf{T}, \mathbf{p})[U]$  is not void. This means that there are  $(e_1, v_1)$  in  $C_1 \cap U$  and  $(e_2, v_2)$  in  $C_2 \cap U$  such that  $(\mathbf{T}, \mathbf{p})(e_1, v_1) = (\mathbf{T}, \mathbf{p})(e_2, v_2)$ . We arrived at the contradiction that  $(\mathbf{T}, \mathbf{p})$  is not injective in any neighbourhood of  $(e_c, v_c)$ ; as a consequence,  $(e_c, v_c)$  cannot be in  $R$ .

## 7. Multicomponent substances

A multicomponent substance, besides its specific internal energy and specific volume, is characterized by the concentrations of the substances that is constituted of. The concentrations of an  $n$ -component substance are in (notation:2.2.)

$$C_{n-1} := \{c = (c_1, \dots, c_n) \in D_{n-1} \mid 0 < c_i < 1, (i = 1, \dots, n)\}.$$

**Definition 10.** An  $n$ -component substance is a triplet  $(D, \mathbf{s}, R)$ , where

(i)  $D$ , called the *constitutive domain*, is a non-void subset of  $(J/kg)^+ \times (m^3/kg)^+ \times C_{n-1}$ ;

(ii)  $\mathbf{s} : D \rightarrow (J/kgK)$ , the *specific entropy*, is continuously differentiable and its first and second partial derivatives are everywhere positive,

(iii)  $R$ , the *regular constitutive domain*, is an open subset, consisting of the elements  $(e, v, c) \in D$  such that  $\mathbf{s}$  is twice continuously differentiable at  $(e, v, c)$  and  $\mathbf{s}''(e, v, c)$  is negative definite.

**Remarks 9.** (i) The temperature and the pressure of the substance are defined from the first and second partial derivative of  $\mathbf{s}$  by the usual formulae given in Remark 1:

$$\frac{1}{\mathbf{T}} = \frac{\partial \mathbf{s}}{\partial e}, \quad \frac{\mathbf{p}}{\mathbf{T}} = \frac{\partial \mathbf{s}}{\partial v}.$$

(ii) Moreover, one frequently assumes  $\frac{\partial \mathbf{s}}{\partial c_i}$  equals  $\frac{\mu_i}{\mathbf{T}}$  where  $\mu_i$  is the chemical potential of the  $i$ -th component ([11]); however, this is not right, because such a partial derivative does not exist: the concentrations cannot vary independently (see 2.2.(iii)).

We can fix an  $e$  and  $v$  and take the derivative of the function  $C_{n-1} \rightarrow (J/kgK)$ ,  $c \mapsto \mathbf{s}(e, v, c)$ , denoted by  $\frac{\partial \mathbf{s}(e, v, c)}{\partial c}$ ; it is a linear map from  $\mathbf{D}_{n-1}$  into  $(J/kgK)$ . Then we can write that

$$\frac{\partial \mathbf{s}}{\partial c} = \left( \left( \frac{\mu_1}{\mathbf{T}}, \dots, \frac{\mu_n}{\mathbf{T}} \right) \right).$$

The relations above do not determine uniquely the chemical potentials. The uniqueness follows from the requirement

$$\sum_{i=1}^n \mu_i \mathbf{c}_i = \mathbf{e} + \mathbf{p}v - \mathbf{T}\mathbf{s}$$

where  $\mathbf{c}_i$  is the  $i$ -th concentration function which assigns  $c_i$  to  $(e, v, c)$ .

(iii) In the following we use the independent concentrations  $\tilde{c} := (c_1, \dots, c_{n-1})$ , and we denote by a tilde that a function of concentrations is considered to be a function of the chosen  $n - 1$  independent concentrations; e.g.

$$\tilde{\mathbf{s}}(e, v, \tilde{c}) = \mathbf{s} \left( e, v, c_1, \dots, c_{n-1}, 1 - \sum_{i=1}^{n-1} c_i \right).$$

Furthermore we put

$$\begin{aligned} \mu &:= (\mu_1, \dots, \mu_n), \\ \gamma_i &:= \mu_i - \mu_n \quad (i = 1, \dots, n-1), \quad \gamma := (\gamma_1, \dots, \gamma_{n-1}). \end{aligned}$$

Then  $\partial \tilde{\mathbf{s}} / \partial c_i = \tilde{\gamma}_i$  ( $i = 1, \dots, n-1$ ) and note that the injectivity of  $\mathbf{s}'$  is equivalent to the injectivity of  $(\mathbf{T}, \mathbf{p}, \gamma)$ .

(iv) The negative definiteness of  $\mathbf{s}''(e, v, c)$  is equivalent to the negative definiteness of  $\tilde{\mathbf{s}}''(e, v, \tilde{c})$  which is an  $(n+1) \times (n+1)$  matrix. If one formally took the partial derivatives of  $\mathbf{s}$  according to all the concentrations ([11]) then  $\mathbf{s}''(e, v, c)$  would be an  $(n+2) \times (n+2)$  matrix, whose negative definiteness would be a stronger requirement.

We can repeat word by word Definition 2 and Proposition 1 for phases of a multicomponent substance. In a phase  $F$  of a multicomponent substance specific internal energy, specific volume and the concentrations are given as continuously differentiable functions of temperature, pressure and  $n - 1$  chemical potential differences; consequently, the  $n$ -th chemical potential is a function of the listed

intensive variables. If  $\mu_n$  denotes this function then the Gibbs-Duhem relations read in our notations as follows:

$$\begin{aligned} \frac{\partial \mu_n(F)}{\partial T} \circ (\mathbf{T}, \mathbf{p}, \gamma) &= -s|_F, & \frac{\partial \mu_n(F)}{\partial p} \circ (\mathbf{T}, \mathbf{p}, \gamma) &= v|_F, \\ \frac{\partial \mu_n(F)}{\partial \gamma_i} \circ (\mathbf{T}, \mathbf{p}, \gamma) &= \mathbf{c}_i|_F \quad (i = 1, \dots, n-1). \end{aligned}$$

Definitions 3 and 4 can be repeated for zeroth-order and second-order phase connections of a multicomponent substance. To avoid the possibility of confusion of indices, we shall write parantheses for the indices regarding two phases.

First-order phase connections are defined similarly to Definition 8, according to the sense, as detailed below.

**Definition 11.** Let  $F_{(1)}$  and  $F_{(2)}$  be phases of a multicomponent substance. If

$$\begin{aligned} S_{(1)} := \{ & (e_{(1)}, v_{(1)}, c_{(1)}) \in F_{(1)} \setminus \overline{F_{(2)}} \mid \text{there is a } (e_{(2)}, v_{(2)}, c_{(2)}) \in F_{(2)} \setminus \overline{F_{(1)}}, \\ & (\mathbf{T}, \mathbf{p}, \mu)(e_{(1)}, v_{(1)}, c_{(1)}) = (\mathbf{T}, \mathbf{p}, \mu)(e_{(2)}, v_{(2)}, c_{(2)}) \}, \end{aligned}$$

$$\begin{aligned} S_{(2)} := \{ & (e_{(2)}, v_{(2)}, c_{(2)}) \in F_{(2)} \setminus \overline{F_{(1)}} \mid \text{there is a } (e_{(1)}, v_{(1)}, c_{(1)}) \in F_{(1)} \setminus \overline{F_{(2)}}, \\ & (\mathbf{T}, \mathbf{p}, \mu)(e_{(1)}, v_{(1)}, c_{(1)}) = (\mathbf{T}, \mathbf{p}, \mu)(e_{(2)}, v_{(2)}, c_{(2)}) \} \end{aligned}$$

are not void then the pair  $(S_{(1)}, S_{(2)})$  is called a *first-order phase connection* between  $F_{(1)}$  and  $F_{(2)}$ .

Copying the proof of Proposition 2, replacing  $(\mathbf{T}, \mathbf{p})$  with  $(\tilde{\mathbf{T}}, \tilde{\mathbf{p}}, \tilde{\gamma})$  and  $\mu$  with  $\mu_n$ , we can demonstrate that  $S_{(1)}$  and  $S_{(2)}$  as well as their image by  $(\tilde{\mathbf{T}}, \tilde{\mathbf{p}}, \tilde{\gamma})$  are hypersurfaces. This latter is determined by a system of partial differential equations which, in general, is too complicated for being successfully applicable.

Finally, the critical points of two phases with a first-order phase connection of a multicomponent substance are defined as in Definition 9, and we can prove similarly that a critical point is in the second order phase connection of the two phases.

## 8. Discussion

Phases are defined to be convenient open subsets in the space of extensive parameters.

If two phases have a phase connection then phase transition may occur between the two phases, i.e. there are processes starting from one of the phases and ending in the other.

Zeroth-order, first-order and second-order phase connection have been defined. Two phases can have more phase connections. For example, the liquid phase and the gaseous phase of a substance have a zeroth-order phase connection (over the critical point), a second-order phase connection (the critical point) and a first-order phase connection (under the critical point).

A zeroth-order phase connection is a subset of the regular domain; in a zeroth-order phase transition everything changes continuously (continuous phase transition).

A second-order phase connection is a subset of the boundaries of two phases outside the regular domain; in a second-order phase transition the state of the substance changes continuously but some quantities change discontinuously (gradual phase transition).

A first-order phase connection is in different disjoint parts of two phases; in a first-order phase transition the state of the substance changes discontinuously (abrupt phase transition).

Then it is clear that the sequence of classes zeroth-order, second-order, first-order is more natural in this respect than the one indicated by the numerals zeroth, first, second.

The relation between Tisza's and Ehrenfest's ideas are clearly exhibited by our treatment. Since it is based on continuous differentiability, third-order and higher order phase connections make no sense in it. These notions would be meaningful if the regular constitutive domain were defined to be the set where specific entropy is smooth (infinitely differentiable). Then Definition 4 would describe second- or-higher-order phase connection; however, in general, a definite order could not be assigned to such a phase connection. In special cases we could define an  $m$ -th order phase connection by modifying (iii) in Definition 8:  $s$  is  $(m - 1)$  times continuously differentiable on  $C$  without being  $m$  times continuously differentiable, and its  $(m - 1)$ -th derivative is continuously differentiable on  $C$  from both sides. It seems, however, that practice does not demand the notion of higher order phase connections.

Phase connections of multicomponent substances, in principle, are similar to those of single-component substances. However, in practice, they are much more complicated: instead of curves we have to deal with multidimensional surfaces. Moreover, the chemical potentials of the components are not easily measurable quantities, thus the surface in the  $(T - p - \gamma)$ -space, corresponding to a first order phase connection (analogue of the phase line described by the Clausius-Clapeyron equation), besides being described by a system of partial differential equations, has no direct physical meaning. That is why the question of first-order phase connections of multicomponent substances is discussed frequently from different points of view ([12]).

## References

- [1] L. Tisza, *Generalized Thermodynamics*, M.I.T Press, Cambridge, Mass 1966.
- [2] H.B.Callen, *Thermodynamics*, Wiley and Sons, New York 1960.
- [3] R.Hagan and J.Serrin, Dynamic Changes of Phase in a Van der Waals Fluid, *New Perspectives of Thermodynamics*, Springer, Berlin 1986.
- [4] M.E.Gurtin, *Arch.Rat.Mech.Anal.* **123** (1993), 306–333.
- [5] M.Brokate, N.Kenmochi, I.Müller, J.E.Rodriguez, C.Verdi, *Phase Transitions and Hysteresis*, Springer-Verlag, Berlin 1994.
- [6] J.M.Ball, P.J.Holmes, R.D.James, R.L.Pego, *J.Nonlin.Sci.* **1** (1991), 17–70.
- [7] Fu-Ming Tao and E.A.Masson, *J. Chem. Phys.* **100** (1994), 9075–9087.
- [8] T. Matolcsi, *Arch.Rat.Mech.Anal* **91** (1986), 99–118.
- [9] T. Matolcsi, *Spacetime without Reference Frames*, Akadémiai Kiadó, Budapest 1993.
- [10] C.Truesdell, S.Bharatha, *Classical Thermodynamics as a Theory of Heat Engines*, Springer, Berlin 1977.
- [11] H. Kreutzer, *Non-equilibrium Thermodynamics and its Statistical Foundations*, Clarendon Press, Oxford 1981.
- [12] P.H.E.Meijer, *J.Chem.Phys.* **101** (1994) 5140–5147.

T. Matolcsi  
Departement of Applied Analysis  
Eötvös Loránd University  
H-1088 Budapest, Muzeum krt.6–8.  
e-mail: matolcsi@ludens.elte.hu

(Received: June 29, 1995; revised: May 25, 1996)