Citation:

Contribution to the theory of corresponding states, in:
KNAW, Proceedings, 17 II, 1914, pp. 840-845

Physics. — *"Contribution to the theory of corresponding states."* By Mrs. T. EHRENFEST-AFANASSJEWA. D. Sc. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of September 26, 1914).

§ 1. MESLIN [1]) has tried to demonstrate that every equation of state which contains the same number of material constants as variables, is to be reduced to a universal shape (i. e. to such a form that no parameters occur any more which vary with the substance), if the variables are replaced by their relations to suitable special values, which may be designated as "corresponding" for different substances.

On closer investigation it appears, however, that the equality of the number of the parameters and that of the variables is neither necessary nor sufficient for the existence of corresponding states.

A method will be given here to decide whether a given equation allows the existence of corresponding states. This method furnishes at the same time the possibility to calculate the eventually corresponding values of the variables for different substances.

§ 2. In the first place we shall define the term "corresponding states" in a somewhat more general form. Let an equation be given between a system of n variables: $x_1, x_2, \ldots x_n$ and a number m of such parameters: $C_1, C_2, \ldots C_m$ that they can vary with change of definite circumstances (*for example* of the substance).

Let an *arbitrary* system of special values: $x_1', x_2', \ldots x_n'$ (we shall briefly denote it by x_i') of the variables x_i be known, which satisfies this equation for definite special values C_i' of the parameters C_i.

Let us introduce the following new variables:

$$y_1 = \frac{x_1}{x_1'} \quad , \quad y_2 = \frac{x_2}{x_2'}, \ldots y_n = \frac{x_n}{x_n'} \quad . \quad . \quad . \quad . \quad (1)$$

All the constants S_j of the thus transformed equation can be calculated as functions of the former constant coefficients, of the values C_i' and of the values x_h'.

When the parameters C_i assume other special values C_i'', other systems of special values of the variables will satisfy the original equation.

The case may occur that there is among them such a system of values:

[1]) MESLIN: Sur l'équation de VAN DER WAALS et la démonstration du théorème des états correspondants C.R. 1893, p. 135.

$$x_1'', x_2'', \ldots x_n''$$

that on the substitution of

$$y_i = \frac{x_i}{x_i''} \quad \ldots \ldots \ldots \ldots \quad (2)$$

for x_i, the constants of the transformed equation assume exactly the same numerical values S_j as in the first case. We call *such values* $x_1'', x_2'', \ldots x_n$ *correspondent to the values* $x_1', x_2', \ldots x_n$, and the *state* defined by the values x_i'', *correspondent* to that defined by the values x_i (or corresponding to it).

The form to which the given equation is reduced in this case by the substitution $y_i = \frac{x_i}{x_i}$, resp. $y_i = \frac{x_i}{x_i''}$, will be indicated by the word *universal*.

§ 3. When for the system x_i' the system x_i'' corresponding to it has been given, the system x_{i1}'' can be easily calculated, which corresponds with every other system x_{i1}' of x_i values, which satisfies the equation in the first case, by the aid of the following equations:

$$\frac{x_i'}{x_{i1}'} = \frac{x_i''}{x_{i1}''}.$$

Indeed the values x_i' resp. x_i'' satisfy the original equation, when the parameters C_i assume in it the values C_i' resp. C_i''. When now the substitution

$$y_i = \frac{x_i}{x'_{i1}} \quad \ldots \ldots \ldots \ldots \quad (3)$$

has been carried out, the constants S_i which we have calculated, assume other values, e. g. S_{i1}, and we must now find the values x_{i1}'', which keep the quantities S_{i1} invariant on substitution of C_i'' for C_i', when the substitution:

$$y_i = \frac{x_i}{x_{i1}''} \quad \ldots \ldots \ldots \ldots \quad (4)$$

is carried out.

The values x_i', however, satisfying the given equation,

$$y_{i1}' = \frac{x_i'}{x_{i1}'}$$

satisfy the transformed equation. The constants of the transformed equation do not change, when

$$\frac{x_i''}{x_{i1}''} = \frac{x_i'}{x_{i1}'}$$

is substituted for y_{i1}'.

The fraction:

$$\frac{x_i''}{x_{i1}''} = \frac{x_i'}{x_{i1}'}$$

belongs therefore to the corresponding values x_i'', hence x_{i1}' corresponds to x_{i1}''.

Hence it is proved that *in the case of a system of values corresponding to a system of solutions, there also exists a system corresponding to every other system of solutions* (when C_i' have been replaced by C_i'').

§ 4. To find a system x_i'', if the system x_i' has been given, we take into account every product of powers of the variables:

$$P_i = x_1^{a_{i1}} x_2^{a_{i2}} \ldots\ldots x_n^{a_{in}} \quad \ldots\ldots \quad (6)$$

which appears as separate argument in the given equation. We shall therefore write the given equation as follows:

$$\Phi\,(K_1 P_1, K_2 P_2, \ldots\ldots K_k P_k ; L_1, L_2 \ldots\ldots L_l) = 0 \quad \ldots \quad (7)$$

K_i and L_i are constants with relation to x_i, L_i are those constants which do not occur as *factor of* P_i, but *in any other way.* Among the K_i and L_i are therefore also included the variable parameters (for their functions).

Let us put that the constants K_i, L_i in the first, resp. second case have the special values:

$$K_i', L_i', \text{ resp. } K_i'', L_i''$$

(those among them which are independent of C_i, have the same values in both cases); they are to be considered as *given.* We can write every variable also in the following way:

$$x_i = x_i' \frac{x_i}{x_i'} = x_i' y_i.$$

If we put them in this form in the equation (7), it assumes the following form:

$$\Phi\,(Q_1' P_1(y), \ldots\ldots Q_k' P_k(y) ; L_1', \ldots\ldots L_l') = 0 \quad \ldots \quad (8)$$

in which

$$Q_i' = K_i' P_i' \quad \ldots\ldots \quad (9)$$

$$P_i' = x_1'^{a_{i1}} x_2'^{a_{i2}} \ldots\ldots x_n'^{a_{in}} \quad \ldots\ldots \quad (10)$$

$$P_i(y) = y_1^{a_{i1}} y_2^{a_{i2}} \ldots\ldots y_n^{a_{in}} \quad \ldots\ldots \quad (11)$$

Now it is evidently the question to find such values x_i'' that when C_i' is replaced by C_i'' and x_i' by x_i'', all the constants Q_i and L_i — eventually with the exception of one factor, by which all the terms of the equation can be divided — assume the same values.

When we carry out this division — let the factor in question be R (it can be both one of the Q_i and one of the L_i) in all $k+l-1$ constants remain, which can have four different forms:

$$Q_j\,,\frac{Q_g}{R}\;;\;L_h\,,\frac{L_j}{R}.$$

The required x_i'' must now satisfy the following equations:

$$\left.\begin{array}{l} Q_f' = Q_f'' \\ \dfrac{Q_g'}{R'} = \dfrac{Q_g''}{R''} \\ \dfrac{L_j'}{R'} = \dfrac{L_j''}{R''} \end{array}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

and besides the following equations must hold:

$$L_h' = L_h'' \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (13)$$

The number of equations (12), in which x_i'' occurs, is quite independent of the number of m of the variable parameters C_i.

When all equations (13) are satisfied, and all those among the equations (12) which do not contain x_i'', the three following cases can occur.

1. Equations (12) are in conflict with each other (a group of s of the sought values is defined by more than s independent equations.

2. They have *one*, or *a finite number* of systems of solutions. (It is required, though not sufficient for this that the number of independent equations in which x_i'' occurs, is equal to n. Hence m must not be greater than n).

Which of the systems of solutions corresponds with the given system x_i', has to be decided by a further investigation in every separate case.

This is the case in which we have corresponding states.

3. They have an infinite number of systems of solutions. (It is required for this that n is greater than the number of the equations that are mutually independent). In this case we may speak of corresponding states for the same conditions (e. g. for the same substance).

§ 5. We shall now examine how Meslin has come to another conclusion. Meslin starts from the conviction that all the constants of an equation are independent of the choice of the unities, when every variable in the equation has been divided by a special value of it. This is perfectly correct. It is also true, as we have seen, that every equation can be reduced to a form as meant here.

It is however not true that those constants that do not change through exchange of the unities, would also have to be unive sal.

MESLIN seems to be not quite free from a confusion, which is indeed pretty widely spread: between the change of a number occurring in an equation *through change of unities*, ("formal" change) and its change *through transition to other conditions* (to other specimens of the quantities which are measured by this number) ("material" change).

In connection with this the assertion that in case of an equal number of variables and parameters the latter can always be completely expressed in the former, is to be rejected.

§ 6. We shall illustrate what we have discussed by examples, which though fictitious, are as simple as possible. Their claim to physical signification, can indeed always be vindicated in this way that they are interpreted as equations for the geometric shape of some physical system.

1. $y = ax^2 + x + b \qquad (n = 2, \quad m = 2).$

a. Introduction of special values of the variables

$$y_0 \frac{y}{y_0} = a x_0^2 \left(\frac{x}{x_0}\right)^2 + x_0 \frac{x}{x_0} + b$$

b. Division by $Q_1 = y_0$:

$$\frac{y}{y_0} = a \frac{x_0^2}{y_0} \left(\frac{x}{x_0}\right)^2 + \frac{x_0}{y_0} \frac{x}{x_0} + \frac{b}{y_0}$$

c. Determination of the numerical values of the special values of the variables satisfying the equation and of the coefficients:

$$x_0 = -\frac{1}{a} \quad , \quad y^0 = b$$

$$\frac{a x_0^2}{y_0} = \frac{1}{ab}$$

$$\frac{x_0}{y_0} = -\frac{1}{ab}$$

$$\frac{b}{y^0} = 1.$$

d. Determination of the system of corresponding values:

$\frac{a' x_0'^2}{y_0'} = \frac{1}{ab}$	$y_0 = b'$
$\frac{x_0'}{y_0'} = -\frac{1}{ab}$	$x_0' = -\frac{b'}{ab}$
$\frac{b'}{y_0'} = 1$	$\frac{a' x_0'^2}{y_0'} = \frac{a' b'}{a^2 b^2} = \frac{1}{ab}$,

from which would follow that $a'b' = ab$, which would be possible only when we have really but one independent parameter.

It follows, however, from the thesis of § 3 that if for *one* system of solutions there is not to be found a corresponding one, there does not exist one for any other system of solutions.

Hence the given equation cannot be reduced to a universal form.

2. $y = a^2x^2 + abx + b^2 \qquad (n = 2\ ,\quad m = 2)$

a. $$y_0 \frac{y}{y_0} = a^2x_0^2\left(\frac{x}{x_0}\right)^2 + abx_0\frac{x}{x_0} + b^2$$

b. $$\frac{y}{y_0} = \frac{a^2x_0^2}{y_0}\left(\frac{x}{x_0}\right)^2 + \frac{abx_0}{y_0}\frac{x}{x_0} + \frac{b^2}{y_0}$$

c. $$y_0 = -b^2 \quad ; \quad x_0 = \frac{-b}{a}$$

$$\frac{a^2x_0^2}{y_0} = 1 \quad ; \quad ab\frac{x_0}{y_0} = 1 \quad ; \quad \frac{b^2}{y_0} = -1$$

d. $$y_0' = -b'^2 \quad ; \quad x_0' = -\frac{b'}{a'}.$$

3. $y = ax^2 + x \qquad (n = 2\ ,\quad m = 1)$

a. $$y_0\frac{y}{y_0} = ax_0^2\left(\frac{x}{x_0}\right)^2 + x_0\frac{x}{x_0}$$

b. $$\frac{y}{y_0} = \frac{ax_0^2}{y_0}\left(\frac{x}{x_0}\right)^2 + \frac{x_0}{y_0}\frac{x}{x_0}$$

c. $$x_0 = \frac{1}{a} \quad ; \quad y_0 = \frac{2}{a}$$

$$\frac{ax_0^2}{y_0} = \frac{1}{2} \quad ; \quad \frac{x_0}{y_0} = \frac{1}{2}$$

d. $$x_0' = \frac{1}{a'} \quad ; \quad y_0' = \frac{2}{a'}.$$

4 [1]. $pv = A + BT + CT^2 \qquad (n = 3,\ m = 3)$

a. $$p_0v_0\frac{p}{p_0}\frac{v}{v_0} = A + BT_0\frac{T}{T_0} + CT_0^2\left(\frac{T}{T_0}\right)^2$$

d. $$p_0v_0 = p_0'v_0' \quad ; \quad A = A' \quad ; \quad BT_0 = B'T_0' \quad ; \quad CT_0^2 = C'T_0'^2.$$

As $\frac{B}{B'}$ is independent of $\frac{C}{C'}T_0^2$, the two last comparisons are contradictory, so that even if $A = A'$, we should not have corresponding states.

Leiden, August 1914.

[1]) This example fails in the Dutch text.