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**Chemistry.** — “*Pressure- and temperature-coefficients, volume- and heat-effects in bivariant systems.*” By P. H. J. HOENEN, S.J.  
(Communicated by Prof. SCHREINEMAKERS.)

(Communicated at the meeting of Sept. 27, 1919).

In a previous communication<sup>1)</sup> we developed a general law (of which the so-called BRAUN'S law is a particular case) giving a relation between the pressure- and temperature-coefficients of the solubility of several solid substances, with which a solvent is saturated, and the heat of solution and volume increase accompanying the solution of these substances. In the present communication we shall attempt to find a similar relation for arbitrary bivariant systems.

### I. *Heterogeneous Equilibria.*

1. With  $n$  components we have a bivariant system in the usual sense of the term, when there are  $n$  coexisting phases. In this case there are two independent variables, e.g., pressure and temperature. We can, however, even when there are fewer than  $n$  phases present, retain only these two as independent variables, if we subject all variations in the system to the condition that the composition of the whole remains constant. Then, no matter how many phases we have, provided the number is not more than  $n$ , pressure and temperature alone remain the independent variables.

There must thus be a relation among all the systems. Such systems differ greatly from bivariant systems in the ordinary sense of the term, i.e. from systems with  $n$  phases, in that in the latter case the composition of the phases is separately independent of the composition of the system as a whole. This is not the case with the systems which are only “bivariant with constant total composition.”

We shall illustrate the above by a consideration of the equilibrium equations. We assume that we have  $n$  components in  $l$  phases.

Let the composition of the phases be as follows:

1 <sup>st</sup> phase:	$x_1, y_1, z_1, \dots$
2 <sup>nd</sup> „	$x_2, y_2, z_2, \dots$
• • • • •	• • • • •
$l^{\text{th}}$ „	$x_l, y_l, z_l, \dots$

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<sup>1)</sup> See the preceding communication in these Proceedings.

The composition of each phase is given in terms of the absolute quantity in mols of each component. Between these quantities the following relations subsist:

$$\left. \begin{aligned} x_1 + x_2 + \dots + x_l &= X \\ y_1 + y_2 + \dots + y_l &= Y \\ z_1 + z_2 + \dots + z_l &= S \\ \dots & \dots \end{aligned} \right\} \dots \dots \dots (1)$$

The number of equations in (1) is  $n$ . The quantities  $X, Y, S, \dots$ , which determine the total composition, are to be considered constant.

If we represent the  $\zeta$ -functions of the separate phases by  $Z_1, Z_2, \dots, Z_l$ , the equilibrium conditions are:

$$\left. \begin{aligned} \frac{\partial Z_2}{\partial x_2} - \frac{\partial Z_1}{\partial x_1} &= 0 & ; & & \frac{\partial Z_3}{\partial x_3} - \frac{\partial Z_1}{\partial x_1} &= 0 & ; \dots & & \frac{\partial Z_l}{\partial x_l} - \frac{\partial Z_1}{\partial x_1} &= 0 ; \\ \frac{\partial Z_2}{\partial y_2} - \frac{\partial Z_1}{\partial y_1} &= 0 & ; & & \frac{\partial Z_3}{\partial y_3} - \frac{\partial Z_1}{\partial y_1} &= 0 & ; \dots & & \frac{\partial Z_l}{\partial y_l} - \frac{\partial Z_1}{\partial y_1} &= 0 ; \\ \dots & \dots & & & \dots & \dots & & & \dots & \dots \end{aligned} \right\} \dots \dots (2)$$

The number of equations (2) is  $n(l-1)$ .

With regard to the form of these equations it may be noted that the expressions on the left are homogeneous functions of degree 0 with respect to the variables  $x_1, y_1, \dots$ , and are thus only dependent on the ratios of these variables to each other (e.g.,  $\frac{y_1}{x_1}, \frac{z_1}{x_1}$ , etc.) and not on the absolute values. Besides  $p$  and  $T$  we have therefore only  $l(n-1)$  unknowns or variables, since in each phase there are only  $n-1$  ratios which determine the composition.

If  $l = n$ , we have  $n(n-1)$  equations (2) with  $n(n-1)$  unknowns (besides  $p$  and  $T$ ). For given values of  $p$  and  $T$  the composition is thus completely determined by these equations and is thus independent of the total composition  $X, Y, \dots$ . Equations (1) serve only for the calculation of the absolute values of  $x_1$ , etc.

If  $l < n$ , we have fewer equations (2) than unknowns which determine the composition of each phase. In this case for the calculation of the composition of the phases we must make use of the equations (1), so that the composition of each phase is dependent on the total composition.

We have, however, always a sufficient number of equations for the calculation of the composition of each phase for a given value of  $p$  and  $T$ , for we have  $n + n(l-1) = nl$  equations in  $nl$  unknown quantities  $x_1, y_1, \dots, x_2, y_2, \dots$  in which  $p$  and  $T$  can be considered as the independent variables.

We have therefore, independently of the number of phases, provided  $l < n$ , a "bivariant system with constant total composition".

2. We shall now investigate for a bivariant system consisting of  $n$  components in  $l$  phases ( $l \geq n$ ) a relation between the pressure- and temperature-coefficients for the transition of the components from one phase to another, and the heat effects and volume changes which accompany this transition.

The composition of the different phases may be represented as before. The  $\zeta$ -function of the system is represented by  $Z$ , the entropy by  $H$ , and the volume by  $V$ . For the separate phases these quantities are represented by  $Z_1, H_1, V_1$ , etc.

We have then:

$$Z = Z_1 + Z_2 + \dots + Z_l.$$

$$V = V_1 + V_2 + \dots + V_l.$$

$$H = H_1 + H_2 + \dots + H_l.$$

These quantities are given as functions of  $p$  and  $T$  and also of  $x_1, y_1, \dots, x_2, y_2, \dots$ , etc. in which  $p$  and  $T$  are the only independent variables. With regard to notation, the following may be remarked. Partial differentiation with respect to one independent variable, the other independent variable alone being kept constant, (i.e., in a state of equilibrium), is indicated by a stroke above the differential coefficient; partial differentiation with respect to one variable, all other variables being considered constant, (in this case heterogeneous equilibrium is not necessarily present) is indicated by the absence of the stroke.

We can establish the desired relations by the method described in a previous communication for an analogous case. We differentiate the equations (2) partially, first with respect to  $p$ , and then with respect to  $T$ . After multiplication by suitably chosen factors the equations are added together. The following, however, is a shorter and, in my opinion, a more elegant method.

We begin with the simple, purely analytical equation:

$$\frac{\partial^2 Z}{\partial T \partial p} = \frac{\partial^2 Z}{\partial p \partial T}$$

This may be written:

$$\frac{\partial \bar{V}}{\partial T} = -\frac{\partial \bar{H}}{\partial p} \quad \text{or} \quad \frac{\partial \bar{V}}{\partial T} + \frac{\partial \bar{H}}{\partial p} = 0 \quad \dots \quad (3)$$

But

$$\frac{\partial \bar{V}}{\partial T} = \frac{\partial V}{\partial T} + \frac{\partial V}{\partial x_1} \left( \frac{\partial x_1}{\partial T} \right) + \frac{\partial V}{\partial x_2} \left( \frac{\partial x_2}{\partial T} \right) \dots + \frac{\partial V}{\partial y_1} \left( \frac{\partial y_1}{\partial T} \right) + \frac{\partial V}{\partial y_2} \left( \frac{\partial y_2}{\partial T} \right) + \dots \quad (4)$$

and

$$\frac{\partial \bar{H}}{\partial p} = \frac{\partial H}{\partial p} + \frac{\partial H}{\partial x_1} \left( \frac{\partial x_1}{\partial p} \right) + \frac{\partial H}{\partial x_2} \left( \frac{\partial x_2}{\partial p} \right) + \dots + \frac{\partial H}{\partial y_1} \left( \frac{\partial y_1}{\partial p} \right) + \frac{\partial H}{\partial y_2} \left( \frac{\partial y_2}{\partial p} \right) + \dots \quad (5)$$

Also

$$\frac{\partial V}{\partial T} = \frac{\partial V_1}{\partial T} + \frac{\partial V_2}{\partial T} + \dots + \frac{\partial V_l}{\partial T}$$

and

$$\frac{\partial H}{\partial p} = \frac{\partial H_1}{\partial p} + \frac{\partial H_2}{\partial p} + \dots + \frac{\partial H_l}{\partial p}$$

As now for a given phase ( $k$ )

$$\frac{\partial V_k}{\partial T} + \frac{\partial H_k}{\partial p} = 0,$$

since

$$\frac{\partial V_k}{\partial T} = \frac{\partial^2 Z_k}{\partial T \partial p} \quad \text{and} \quad \frac{\partial H_k}{\partial p} = - \frac{\partial^2 Z_k}{\partial p \partial T},$$

we have also

$$\frac{\partial V}{\partial T} + \frac{\partial H}{\partial p} = 0.$$

If we add (4) and (5) and take (3) into consideration, we have as a result:

$$\left. \begin{aligned} & \frac{\partial V}{\partial x_1} \left( \frac{\partial x_1}{\partial T} \right) + \frac{\partial H}{\partial x_1} \left( \frac{\partial x_1}{\partial p} \right) + \frac{\partial V}{\partial x_2} \left( \frac{\partial x_2}{\partial T} \right) + \frac{\partial H}{\partial x_2} \left( \frac{\partial x_2}{\partial p} \right) + \dots \\ & \dots + \frac{\partial V}{\partial y_1} \left( \frac{\partial y_1}{\partial T} \right) + \frac{\partial H}{\partial y_1} \left( \frac{\partial y_1}{\partial p} \right) + \frac{\partial V}{\partial y_2} \left( \frac{\partial y_2}{\partial T} \right) + \frac{\partial H}{\partial y_2} \left( \frac{\partial y_2}{\partial p} \right) + \dots = 0 \end{aligned} \right\} \quad (6)$$

From equations (1) we have also

$$\frac{\partial x_1}{\partial T} = - \frac{\partial x_2}{\partial T} - \frac{\partial x_3}{\partial T} \dots - \frac{\partial x_l}{\partial T}$$

$$\frac{\partial x_1}{\partial p} = - \frac{\partial x_2}{\partial p} - \frac{\partial x_3}{\partial p} \dots - \frac{\partial x_l}{\partial p},$$

Similar expressions may be deduced for the quantities  $y_1$ , etc.

On substituting these expressions in (6) we obtain:

$$\left( \frac{\partial V}{\partial x_2} - \frac{\partial V}{\partial x_1} \right) \frac{\partial x_2}{\partial T} + \left( \frac{\partial H}{\partial x_2} - \frac{\partial H}{\partial x_1} \right) \frac{\partial x_2}{\partial p} + \dots$$

$$\dots + \left( \frac{\partial V}{\partial y_2} - \frac{\partial V}{\partial y_1} \right) \frac{\partial y_2}{\partial T} + \left( \frac{\partial H}{\partial y_2} - \frac{\partial H}{\partial y_1} \right) \frac{\partial y_2}{\partial p} + \dots = 0$$

In this equation the expression  $\frac{\partial V}{\partial x_2} - \frac{\partial V}{\partial x_1}$  (which is the same as  $\frac{\partial V_2}{\partial x_2} - \frac{\partial V_1}{\partial x_1}$ ) represents the volume increment associated with the

transition of one mol of the component ( $x$ ) from an infinitely large quantity of the first phase into an infinitely large quantity of the second phase, the variables  $p, T$ , and the other components remaining constant. This volume increase may be denoted by  $V_{x12}$ . The expression  $\frac{\partial H}{\partial x_2} - \frac{\partial H}{\partial x_1}$  represents the heat absorbed in the same operation divided by  $T$ . This heat effect may be denoted by  $Q_{x12}$ . For the corresponding differences for the other phases and components analogous symbols may be used. We have now:

$$\left. \begin{aligned} V_{x12} \frac{\partial x_2}{\partial T} + \frac{Q_{x12}}{T} \frac{\partial x_2}{\partial p} + V_{x13} \frac{\partial x_3}{\partial T} + \frac{Q_{x13}}{T} \frac{\partial x_3}{\partial p} + \dots \\ + \dots V_{y12} \frac{\partial y_2}{\partial T} + \frac{Q_{y12}}{T} \frac{\partial y_2}{\partial p} + \dots \end{aligned} \right\} \dots = 0. \quad (7)$$

This is one of the relations which it was our object to establish. From (6) other  $l-1$  similar relations may be derived, in which the pressure and temperature coefficients of the components of one of the  $l-1$  other phases do not occur. We obtain other less symmetrical relations, when we eliminate for the one component the coefficients for one of the phases, for a second component its coefficients for another phase. If a component is absent in one of the phases, the corresponding coefficients vanish.

*Note I.* If one of the phases consists of all the components, and the other phases are all pure components, then we have the case for which in the previous communication the "generalised BRAUN'S law" was established. If these conditions are introduced into equation (6), an expression of this law results. The verification of this may be left to the reader.

*Note II.* If there are  $n$  components in  $n$  phases, the heat effects and the volume increments occurring in (7) have values which are independent of the total composition. When the number of phases is less than  $n$ , that is, when the equilibrium is merely "bivariant with constant total composition" then the values are functions of the total composition.

*Note III.* In our discussion we have nowhere made use of any explicit relation connecting  $Z$  with the composition. The results are therefore valid also in the case of reacting components.

*Note IV.* The line of argument adopted leads to a similar formula in the case of homogeneous equilibria. This will be discussed in a future communication.

*Katwijk a. d. Rijn, August 1919.*