

Citation:

Hoenen, P.H.J., Extension of the law of Braun, in:
KNAW, Proceedings, 22 II, 1920, Amsterdam, 1920, pp. 531-535

117

Chemistry. — “*Extension of the law of Braun*”. By P. H. J. HOENEN
S.J. (Communicated by Prof. SCHREINEMAKERS).

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

Through the brilliant researches which have been carried out in recent years in the VAN 'T HOFF-Laboratory, attention has again been directed to the so-called BRAUN's law. At present this is generally expressed by the formula

$$\left(\frac{\partial x}{\partial p}\right)_T : \left(\frac{\partial x}{\partial T}\right)_p = -\frac{T\Delta V}{Q}, \quad \dots \quad (1)$$

in which, for the equilibrium solid-liquid, $\left(\frac{\partial x}{\partial p}\right)_T$ represents the pressure coefficient of the solubility, $\left(\frac{\partial x}{\partial T}\right)_p$ the temperature coefficient, Q the differential heat of solution, ΔV the differential increase in volume.

This law of BRAUN is a particular case of a general law which we shall proceed to develop.

1. Let us suppose we have a solution saturated with respect to n solid substances. Let the quantity of solvent be one mol, and let the amount of the dissolved substances, which are present in the saturated solution at pressure p and temperature T , be x, y, z, \dots mols. Then in this case the following relation holds:

$$\left(\frac{\partial x}{\partial p}\right)_T \times \frac{Q_x}{T} + \left(\frac{\partial x}{\partial T}\right)_p \times \Delta V_x + \left(\frac{\partial y}{\partial p}\right)_T \times \frac{Q_y}{T} + \left(\frac{\partial y}{\partial T}\right)_p \times \Delta V_y + \dots = 0 \quad (2)$$

Here Q_x represents the heat necessary for the solution of one mol of the first component in an infinitely large quantity of solvent of the given composition at constant pressure p and temperature T . It is therefore the differential molecular heat of solution of this component. ΔV_x is the corresponding volume increase, i.e., the differential molecular volume increment. The other symbols require no further explanation. If we are dealing with one substance only, (2) becomes:

$$\left(\frac{\partial x}{\partial p}\right)_T \times \frac{Q_x}{T} + \left(\frac{\partial x}{\partial T}\right)_p \times \Delta V_x = 0,$$

This equation is the same as (1). It is therefore obvious that BRAUN'S law is a particular case of (2).

2. We shall first of all establish (2) for the simple case that the solution is saturated with respect to two solid substances only; and we assume further that these two substances together with the solvent are independent components in the sense of the phase rule, so that two degrees of freedom are at our disposal, namely, pressure and temperature. The ζ -function of the liquid phase is represented by Z , those of the solid phases (per mol) by ζ_x and ζ_y . The equilibrium conditions are:

$$\frac{\partial Z}{\partial x} - \zeta_x = 0 \quad \dots \dots \dots (3)$$

$$\frac{\partial Z}{\partial y} - \zeta_y = 0 \quad \dots \dots \dots (4)$$

The left hand side of these equations are functions of x, y, p , and T , of which, however, only two may be varied independently.

By differentiating these equations with respect to p with T constant there results:

$$\frac{\partial^2 Z}{\partial x^2} \frac{\partial x}{\partial p} + \frac{\partial^2 Z}{\partial x \partial y} \frac{\partial y}{\partial p} = - \left(\frac{\partial V}{\partial x} - v_x \right) \dots \dots \dots (3a)$$

$$\frac{\partial^2 Z}{\partial x \partial y} \frac{\partial x}{\partial p} + \frac{\partial^2 Z}{\partial y^2} \frac{\partial y}{\partial p} = - \left(\frac{\partial V}{\partial y} - v_y \right) \dots \dots \dots (4a)$$

The notation here requires no explanation. It may be remarked that the right-hand side of (3a) = $-\Delta V_x$ and that of (4a) = $-\Delta V_y$.

If we differentiate the two equations with respect to T , keeping p constant, we obtain:

$$\frac{\partial^2 Z}{\partial x^2} \frac{\partial x}{\partial T} + \frac{\partial^2 Z}{\partial x \partial y} \frac{\partial y}{\partial T} = \left(\frac{\partial H}{\partial x} - \eta_x \right) \dots \dots \dots (3b)$$

$$\frac{\partial^2 Z}{\partial x \partial y} \frac{\partial x}{\partial T} + \frac{\partial^2 Z}{\partial y^2} \frac{\partial y}{\partial T} = \left(\frac{\partial H}{\partial y} - \eta_y \right) \dots \dots \dots (4b)$$

The right-hand sides of these equations (3b) and (4b) are equal to $\frac{Q_x}{T}$ and $\frac{Q_y}{T}$ respectively.

From these four equations the following relation is derived:

$$\left(\frac{\partial x}{\partial p} \right) \times \frac{Q_x}{T} + \left(\frac{\partial x}{\partial T} \right) \Delta V_x + \left(\frac{\partial y}{\partial p} \right) \frac{Q_y}{T} + \left(\frac{\partial y}{\partial T} \right) \Delta V_y = 0 \quad \dots (5)$$

Proof: From (3a) and (4a) follows, on substituting $\frac{\partial^2 Z}{\partial x^2} = r$, $\frac{\partial^2 Z}{\partial x \partial y} = s$,

$$\frac{\partial^2 Z}{\partial y^2} = t,$$

$$\frac{\partial x}{\partial p} = \frac{s\Delta V_y - t\Delta V_x}{rt - s^2} ; \quad \frac{\partial y}{\partial p} = \frac{s\Delta V_x - r\Delta V_y}{rt - s^2} ;$$

From (3b) and (4b) follows:

$$T \frac{\partial x}{\partial T} = \frac{tQ_x - sQ_y}{rt - s^2} ; \quad T \frac{\partial y}{\partial T} = \frac{rQ_y - sQ_x}{rt - s^2} .$$

Substitution of these values in the left hand side of (5) gives a fraction of which the numerator = 0, while the denominator > 0, if the equilibrium is stable. The equation (5) is thus established.

We may remark that the separate sums, as $\frac{\partial x}{\partial p} \times \frac{Q_x}{T} + \frac{\partial x}{\partial T} \Delta V_x$, are not zero except in the special case when $\frac{Q_x}{Q_y} = \frac{\Delta V_x}{\Delta V_y}$.

3. We shall now attempt to establish the general equation (2). We assume that we have a liquid phase consisting of one mol of solvent and x, y, z, \dots mols of the dissolved substances. At pressure p and temperature T the solution is saturated with respect to these substance. We have thus $n + 1$ components in as many phases and have therefore two degrees of freedom at our disposal.

The equilibrium conditions are (for the notation see above):

$$\left. \begin{aligned} \frac{\partial Z}{\partial x} - \zeta_x &= 0 \\ \frac{\partial Z}{\partial y} - \zeta_y &= 0 \\ \frac{\partial Z}{\partial z} - \zeta_z &= 0 \\ \dots & \dots \end{aligned} \right\} \dots \dots \dots (6)$$

The expressions on the left-hand side of these n equations are again functions of $x, y, z, \dots p$, and T . The last two we consider as independent variables. If we differentiate, first with respect to p alone and then with respect to T alone, we obtain the two sets of equations:

$$\left. \begin{aligned} \frac{\partial^2 Z}{\partial x^2} \frac{\partial x}{\partial p} + \frac{\partial^2 Z}{\partial x \partial y} \frac{\partial y}{\partial p} + \frac{\partial^2 Z}{\partial x \partial z} \frac{\partial z}{\partial p} + \dots &= -\Delta V_x \\ \frac{\partial^2 Z}{\partial x \partial y} \frac{\partial x}{\partial p} + \frac{\partial^2 Z}{\partial y^2} \frac{\partial y}{\partial p} + \frac{\partial^2 Z}{\partial x \partial z} \frac{\partial z}{\partial p} + \dots &= -\Delta V_y \\ \frac{\partial^2 Z}{\partial x \partial z} \frac{\partial x}{\partial p} + \frac{\partial^2 Z}{\partial y \partial z} \frac{\partial y}{\partial p} + \frac{\partial^2 Z}{\partial z^2} \frac{\partial z}{\partial p} + \dots &= -\Delta V_z \\ \dots & \dots \end{aligned} \right\} \dots (6a)$$

$$\left. \begin{aligned} \frac{\partial^2 Z}{\partial x^2} \frac{\partial x}{\partial T} + \frac{\partial^2 Z}{\partial x \partial y} \frac{\partial y}{\partial T} + \frac{\partial^2 Z}{\partial x \partial z} \frac{\partial z}{\partial T} + \dots &= \frac{Q_x}{T} \\ \frac{\partial^2 Z}{\partial x \partial y} \frac{\partial x}{\partial T} + \frac{\partial^2 Z}{\partial y^2} \frac{\partial y}{\partial T} + \frac{\partial^2 Z}{\partial x \partial z} \frac{\partial z}{\partial T} + \dots &= \frac{Q_y}{T} \\ \frac{\partial^2 Z}{\partial x \partial z} \frac{\partial x}{\partial T} + \frac{\partial^2 Z}{\partial y \partial z} \frac{\partial y}{\partial T} + \frac{\partial^2 Z}{\partial z^2} \frac{\partial z}{\partial T} + \dots &= \frac{Q_z}{T} \\ \dots & \dots \end{aligned} \right\} \dots \quad (6b)$$

We have again written ΔV_x , for $\frac{\partial V}{\partial v} - v_x$, etc., and $\frac{Q_x}{T}$ for $\frac{\partial H}{\partial s} - \eta_x$, etc.

If we multiply the first of the equations (6a) by $-\frac{\partial x}{\partial T}$, the second by $-\frac{\partial y}{\partial T}$, etc., the first of equations (6b) by $\frac{\partial x}{\partial p}$, the second by $\frac{\partial y}{\partial p}$, etc. and add together the $2n$ equations, we obtain an equation the right hand side of which is:

$$\frac{\partial x}{\partial p} \times \frac{Q_x}{T} + \frac{\partial x}{\partial T} \Delta V_x + \frac{\partial y}{\partial p} \times \frac{Q_y}{T} + \frac{\partial y}{\partial T} \times \Delta V_y + \dots$$

The left hand side of the resultant equation is zero. This may be shown as follows. Each term of the left hand side contains one of the "unknowns" $\frac{\partial x}{\partial p}$, $\frac{\partial y}{\partial p}$, etc. from the equations (6a). Let us consider

the terms which contain one of these unknowns, e.g., $\frac{\partial x}{\partial p}$. In the summation these terms are contributed (1) by the first terms of the equations (6a) and by no other terms of these equations, (2) by the complete left hand side of the first equation (6b), which was multiplied throughout by $\frac{\partial x}{\partial p}$, and by no other equation of (6b).

The terms involving $\frac{\partial x}{\partial p}$ are therefore:

$$\begin{aligned} -\frac{\partial x}{\partial T} \frac{\partial^2 Z}{\partial x^2}, -\frac{\partial y}{\partial T} \frac{\partial^2 Z}{\partial x \partial y}, -\frac{\partial z}{\partial T} \frac{\partial^2 Z}{\partial x \partial z}, \dots \text{ from (6a) and} \\ \frac{\partial^2 Z}{\partial x^2} \frac{\partial x}{\partial T}, \frac{\partial^2 Z}{\partial x \partial y} \frac{\partial y}{\partial T}, \frac{\partial^2 Z}{\partial x \partial z} \frac{\partial z}{\partial T}, \dots \text{ from (6b),} \end{aligned}$$

all terms being multiplied by $\frac{\partial x}{\partial p}$.

From the structure of equations (6a) and (6b) it appears that the

sum of the factors by which $\frac{\partial x}{\partial p}$ is multiplied is zero, and that the same holds for each of the "unknowns". The left hand side of the resultant equation is therefore shown to be zero. We have then as a result:

$$\frac{\partial x}{\partial p} \times \frac{Q_x}{T} + \frac{\partial x}{\partial T} \Delta V_x + \frac{\partial y}{\partial p} \times \frac{Q_y}{T} + \frac{\partial y}{\partial T} \Delta V_y + \dots = 0,$$

that is, equation (2) results. This is the equation which we set out to establish as an extension of BRAUN'S law.

Note I. It is not necessary that the solvent should be a pure substance. It may be a mixture of different substances of which, however, none occurs in the solid state. With this assumption the above method of proof remains exactly the same, and the validity of the result is unaffected. The quantities Q , etc., have, of course in general different values when the "solvent" is differently constituted.

Note II. In the above treatment we have nowhere made use of any explicit relation connecting Z and the composition. It follows from this that the results are valid both for constant and for reacting components. The only assumption made was that the components were independent in the sense of the phase theory.

Note III. For the general case we can give a demonstration on the lines of that given for the simple case of three components. It would then be seen that we must deal with a state of stable equilibrium. Since the proof is more involved than that given above we do not reproduce it here. In a later communication dealing with a more general problem another proof will be found.

Katwijk a. d. Rijn, August 1919.