Physics. — *"The shape of the empiric isotherm for the condensation of a binary mixture"*. By Prof. J. D. van der Waals.

Let us imagine a molecular quantity of a binary mixture with a mass equal to $m_1(1-x) + m_2 x_1$ at given temperature in a volume, so that part of it is in the liquid state, and the remaining part in the vapour state. Let us put the fraction which is found in the vapour state equal to y. The point that indicates the state of that mixture, lies then on a nodal curve which rests on the binodal curve. Let the end of the nodal line which rests on the liquid branch be denoted by the index 1, and the other end by the index 2. Let us represent the molecular volume of the end 1 by v_1, and the molecular volume of the other end by v_2, then when v represents the volume of the quantity which is in heterogeneous equilibrium:

$$v = v_1(1-y) + v_2 y$$

the constant quantity x being represented by:

$$x = x_1(1-y) + x_2 y.$$

From this we find:

$$dv = (v_2 - v_1)\, dy + (1-y)\, dv_1 + y\, dv_2$$

and

$$0 = (x_2 - x_1)\, dy + (1-y)\, dx_1 + y\, dx_2.$$

By elimination of dy we obtain the equation:

$$- dv = \frac{v_2 - v_1}{x_2 - x_1} \left\{ (1-y)\, dx_1 + y\, dx_2) \right\} - (1-y)\, dv_1 - y\, dv_2.$$

Now in general $dv = \left(\dfrac{dv}{dx}\right)_p dx + \left(\dfrac{dv}{dp}\right)_x dp$. Let us apply this equation for the points 1 and 2 of the binodal curve, and let us take the course going from v_1 to $v_1 + dv_1$ and from v_2 to $v_2 + dv_2$ on the surface for the homogeneous phases. Then:

$$dv_1 = \left(\frac{dv_1}{dx_1}\right)_p dx_1 + \left(\frac{dv_1}{dp}\right)_{hom} dp,$$

and

$$dv_2 = \left(\frac{dv_2}{dx_2}\right)_p dx_2 + \left(\frac{dv_2}{dp}\right)_{hom} dp.$$

The quantities $\left(\dfrac{dv_1}{dx_1}\right)_p$ and $\left(\dfrac{dv_2}{dx_2}\right)_p$ must then be taken along an isobar.

If we substitute the values of dv_1 and dv_2 in the equation for dv, it becomes:

$$- dv = (1-y) \left\{ \left[\frac{v_2 - v_1}{x_2 - x_1} - \left(\frac{dv_1}{dx_1} \right)_p \right] dx_1 - \left(\frac{dv_1}{dp} \right)_{hom} \right\} +$$

$$+ y \left\{ \left[\frac{v_2 - v_1}{x_2 - x_1} - \left(\frac{dv_2}{dx_2} \right)_p \right] dx_2 - \left(\frac{dv_2}{dp} \right)_{hom} \right\}$$

or

$$- \left(\frac{dv}{dp} \right)_{het} = (1-y) \left\{ \left[\frac{v_2 - v_1}{x_2 - x_1} - \left(\frac{dv_1}{dx_1} \right)_p \right] \left(\frac{dx_1}{dp} \right)_{bin} - \left(\frac{dv_1}{dp} \right)_{hom} \right\} +$$

$$+ y \left\{ \left[\frac{v_2 - v_1}{x_2 - x_1} - \left(\frac{dv_2}{dx_2} \right)_p \right] \left(\frac{dx_2}{dp} \right)_{bin} - \left(\frac{dv_2}{dp} \right)_{hom} \right\}$$

Now the factor of $\left(\frac{dx_1}{dp} \right)_{bin} = \frac{v_{21}}{x_2 - x_1} = \left(\frac{d^2 \zeta}{dx_1^2} \right)_{p,T} \left(\frac{dx_1}{dp} \right)_{bin}$, and we find:

$$- \left(\frac{dv}{dp} \right)_{het} = (1-y) \left\{ \left(\frac{d^2 \zeta}{dx_1^2} \right)_{p,T} \left(\frac{dx_1}{dp} \right)_{bin}^2 - \left(\frac{dv_1}{dp} \right)_{hom} \right\} +$$

$$+ y \left\{ \left(\frac{d^2 \zeta}{dx_2^2} \right)_{p,T} \left(\frac{dx_2}{dp} \right)_{bin}^2 - \left(\frac{dv_2}{dp} \right)_{hom} \right\} \quad \ldots \quad (1)$$

If we consider the beginning of the condensation, and so $y = 1$, the above equation becomes:

$$- \left(\frac{dv}{dp} \right)_{het} = \left(\frac{d^2 \zeta}{dx_2^2} \right)_{p,T} \left(\frac{dx_2}{dp} \right)_{bin}^2 - \left(\frac{dv_2}{dp} \right)_{hom}$$

in which we must put $v_2 = v$ and $x_2 = x$. It appears from this equation, that never $- \left(\frac{dv}{dp} \right)_{het} = - \left(\frac{dv}{dp} \right)_{hom}$, and that there must therefore be a leap in the value of $- \frac{dv}{dp}$ or of $- \frac{dp}{dv}$ at the beginning of the condensation, unless there should be cases in which $\left(\frac{d^2 \zeta}{dx^2} \right)_{p,T} \left(\frac{dx}{dp} \right)_{bin}^2$ is equal to 0. The only case in which this is so, is in the critical point of contact. There $\left(\frac{dp}{dx} \right)_{bin} = \infty$ and so $\left(\frac{dx}{dp} \right)_{bin} = 0$. But then there is properly speaking no longer condensation, and the empiric isotherm has disappeared. We might think of a plaitpoint, because $\left(\frac{d^2 \zeta}{dx^2} \right)_{p,T} = 0$ in it, but on the other hand $\left(\frac{dp}{dx} \right)_{bin} = 0$ and $\left(\frac{dx}{dp} \right)_{bin} = \infty$ there. If the limiting value of $\left(\frac{d^2 \zeta}{dx^2} \right)_{p,T} \left(\frac{dx}{dp} \right)_{bin}^2$ or of $\dfrac{\left(\frac{d^2 \zeta}{dx^2} \right)_{p,T}}{\left(\frac{dp}{dx} \right)_{bin}^2}$ is sought, we find by differentiating numerator and deno-

minator twice with respect to x:

$$\frac{\left(\frac{d^2\zeta}{dx^2}\right)_{pT}}{\left(\frac{dp}{dx}\right)^2_{bin}} = \frac{\left(\frac{d^3\zeta}{dx^3}\right)_{pT}}{2\left(\frac{dp}{dx}\right)_{bin}\left(\frac{d^2p}{dx^2}\right)_{bin}} = \frac{\left(\frac{d^4\zeta}{dx^4}\right)_{p,T}}{2\left(\frac{d^2p}{dx^2}\right)^2_{bin}}.$$

In a plaitpoint, besides $\left(\frac{d^2\zeta}{dx^2}\right)_{p,T}$ also $\left(\frac{d^3\zeta}{dx^3}\right)_{p,T} = 0$, but $\left(\frac{d^4\zeta}{dx^4}\right)_{p,T}$ will have a value differing from 0, and so there is a leap in the value of $-\frac{dv}{dp}$ in a plaitpoint too.

As $-\left(\frac{dv}{dp}\right)_{hom}$ must always be positive, also $\left(-\frac{dv}{dp}\right)_{het}$ will always be positive and larger than $\left(-\frac{dv}{dp}\right)_{hom}$ or $\left(-\frac{dp}{dv}\right)_{hom} > \left(-\frac{dp}{dv}\right)_{het}$.

At the beginning of the condensation the empiric curve will ascend less steeply with decrease of volume than that for homogeneous phases.

There are cases in which $-\left(\frac{dv}{dp}\right)_{het} = \infty$, or $\left(-\frac{dp}{dv}\right)_{het} = 0$. 1. on the sides, so for $x = 0$ and $x = 1$. Then $\left(\frac{d^2\zeta}{dx^2}\right)_{pT}$ is infinite, and is represented by the principal term $\left(\frac{MRT}{x(1-x)}\right)$. 2. if on the binodal curve $\frac{dx}{dp}$ is infinite or $\frac{dp}{dx} = 0$; this takes place for those mixtures which behave as a simple substance.

If in equation (1) we put $y = 0$ and $v_1 = v$ and $x_1 = x$ we could derive the same conclusions for the end of the condensation.

The relation between $-\left(\frac{dp}{dv}\right)_{het}$ and $-\left(\frac{dp}{dv}\right)_{hom}$ at the beginning and at the end of the condensation, could be immediately derived by applying the equation :

$$dv = \left(\frac{dv}{dp}\right)_x dp + \left(\frac{dv}{dx}\right)_p dx$$

both for the surface of the homogeneous phases and for that of the heterogeneous phases. If we then take into consideration that $\left(\frac{dv}{dx}\right)_p$ on the heterogeneous surface is equal to $\frac{v_2 - v_1}{x_2 - x_1}$, we find :

$$\frac{v_3 - v_1}{x_2 - x_1} dx + \left(\frac{dv}{dp}\right)_{het} dp = \left(\frac{dv}{dx}\right)_p dx + \left(\frac{dv}{dp}\right)_{hom} dp,$$

and from this the former relation.

From the form for $\left(-\dfrac{dv}{dp}\right)_{het}$ in general, so not only at the begin-ning or at the end of the condensation, we see that the empiric isotherm can have an element in which it has an horizontal direction only when a nodal curve is intersected, at one or the other of whose ends $\left(\dfrac{dx}{dp}\right)_{bin}$ is infinitely large. But as neither the sides nor the nodal curve which runs parallel to the v-axis can be intersected, it would follow that the empiric isotherm can never run horizontally in one of its elements. There *are*, however, cases which form exceptions to this rule. First of all if we widen the idea empiric isotherm, and understand by it the section of a surface // v-axis with the derived surface of the ψ-surface, also in the case of a complex plait. Then there are also nodal curves to points in which the binodal curve passes through the spinodal, and where therefore $\left(\dfrac{dx}{dp}\right)_{bin} = \infty$. But as such equilibria are hidden equilibria, they cannot be realised in spite of this. Instead of this we have rectilinear inter-section of the surface // v-axis with the three phase triangle, and in this part $\left(\dfrac{dv}{dp}\right)_{het}$ is, of course, again infinitely large. But secondly, and this is a case which might, indeed, be realised, the binodal curve has a point in which $\left(\dfrac{dx}{dp}\right)_{bin} = \infty$, when this point is a plait-point which with increasing or decreasing temperature will become a hidden plaitpoint. This is a limiting form of the first mentioned case, in which the three phase triangle was intersected. Then the three phase triangle has contracted to a single line, and the above mentioned straight line has contracted to a single point. Then there is, of course, a point of inflection of the empiric isotherm in that point. With larger volumes it is curved negatively, with smaller volumes positively.