ON A PROPERTY OF THE PRESSURE-VOLUME DIAGRAM

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In a recent article,¹ Duhem has shown that, if a network of limiting lines of the binary system formed by means of two liquefiable gases be traced in the pressure-temperature plane, such a network will enable us to determine without difficulty the concentrations of the two phases which can coexist at a given temperature and under a given pressure. I wish to call attention to the use which can be made of the corresponding network of limiting lines in the volume-pressure plane.

To a mixture of two liquefiable gases of mean concentration $S = \frac{\mathfrak{M}_2}{\mathfrak{M}_1}$, $\mathfrak{M}_1$ and $\mathfrak{M}_2$ being the masses of the two components, there corresponds, in the volume-pressure plane, a certain limiting line.² This limiting line is divided into two parts, called respectively dew line and boiling line, the point of division being the point whose coordinates are the critical specific volume and the critical pressure of the mixture of mean concentration S .

Through each point of the volume-pressure plane there passes an isotherm of the mixture of mean concentration S . Thus, to each point of the v - Π plane, there correspond, not only its coordinates v and Π , but also a mean concentration S , which can be chosen at pleasure, and a temperature T , which is determined by the choice of S .

From this it follows that the abscissa of a point P on a dew line of the mixture of mean concentration S is equal to the specific volume of a vapor phase of concentration S , when that

¹ Jour. Phys. Chem. 5, 91 (1901).

² Cf. Duhem. Traité élémentaire de Mécanique chimique, 4, 144.

phase is under a pressure Π , equal to the ordinate of P , and at a temperature T , equal to the temperature of the isotherm, of the mixture S , which passes through P .

Similarly, the abscissa of a point Q on the boiling line of the mixture of mean concentration S is equal to the specific volume of a liquid phase of concentration S , when that phase is under a pressure Π , equal to the ordinate of Q , and at a temperature T , equal to the temperature of the isotherm, of the mixture S , which passes through Q .

Let us suppose that there has been drawn in the volume-pressure plane a network of limiting lines corresponding to binary systems of different mean concentrations, and let us consider two phases in equilibrium at the temperature T and under the pressure Π . As Duhem has shown, the network of limiting lines in the T - Π plane will enable us to determine the concentrations S_1 and S_2 of the two phases, vapor and liquid.

Turn now to the volume-pressure diagram. The point on the dew line of the mixture S_1 whose ordinate is Π will have an abscissa which we shall denote by v_1 . v_1 will be the specific volume of the vapor phase in our two-phase system. The temperature T of the system is the same as the temperature of the isotherm of the mixture S_1 , which passes through the point (v_1, Π) .

Similarly, let us denote by v_2 the abscissa of the point of the boiling line of the mixture S_2 , whose ordinate is Π . v_2 will be the specific volume of the liquid phase in our two-phase system. The temperature T of the system is the same as the temperature of the isotherm of the mixture S_2 which passes through the point (v_2, Π) .

If we denote the masses of the phases by M_1 and M_2 , and the mean specific volume by v , we have the equation

$$v = \frac{M_1 v_1 + M_2 v_2}{M_1 + M_2}. \quad (1)$$

We may now restate our results in the following manner: Given a two-phase system in equilibrium at the temperature T and under the pressure Π . From the network of limiting lines

in the temperature-pressure plane, we determine S_1 and S_2 , the concentrations of the two phases, vapor and liquid. Through the point (τ, Π) , which is supposed to be known, draw a line parallel to the axis of volumes. This line intersects the dew line of the mixture S_1 at a point (τ_1, Π) and the boiling line of the mixture S_2 at a point (τ_2, Π) . τ_1 and τ_2 are the specific volumes of the two phases, vapor and liquid. Finally, equation 1 shows that the point (τ, Π) divides the line $(\tau_2, \Pi), (\tau_1, \Pi)$ in the ratio of the masses of the phases: $M_1 : M_2$.

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