ON CLAPEYRON'S EQUATION

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Consider at the temperature T and under the pressure Π a system whose energy, entropy and volume we shall denote by E , H and V . For a reversible change which leaves the mass of the system unchanged we have the well-known equation

$$dE = T dH - \Pi dV. \quad (1)$$

The total thermodynamic potential Φ is defined by the equation

$$\Phi = E - TH + \Pi V. \quad (2)$$

Making use of equation 1 we obtain

$$d\Phi = -H dT + V d\Pi. \quad (3)$$

Suppose that the system under consideration is a univariant system. In that case Π and T are no longer independent variables; one is a function of the other, so that we may write

$$\Pi = f(T). \quad (4)$$

Equation 1 shows that if we assume E to be a function of H and V , Π and T are also functions of H and V and are given by the equations

$$\frac{\partial E}{\partial H} = T, \quad \frac{\partial E}{\partial V} = -\Pi. \quad (5)$$

If equation 4 is to hold, the Jacobian of Π and T with respect to H and V must vanish. That is to say, equation 4 is equivalent to the equation

$$\begin{vmatrix} \frac{\partial \Pi}{\partial H} & \frac{\partial \Pi}{\partial V} \\ \frac{\partial T}{\partial H} & \frac{\partial T}{\partial V} \end{vmatrix} = 0. \quad (6)$$

For the system under consideration, the thermodynamic potential Φ is also a function of Π or of T . To show this it will be sufficient to prove that

$$\begin{vmatrix} \frac{\partial \Phi}{\partial H} & \frac{\partial \Phi}{\partial V} \\ \frac{\partial T}{\partial H} & \frac{\partial T}{\partial V} \end{vmatrix} = 0. \quad (7)$$

If we make use of equations 2 and 5, this determinant takes the form

$$\begin{vmatrix} -H \frac{\partial T}{\partial H} + V \frac{\partial \Pi}{\partial H} & -H \frac{\partial T}{\partial V} - V \frac{\partial \Pi}{\partial V} \\ \frac{\partial T}{\partial H} & \frac{\partial T}{\partial V} \end{vmatrix}.$$

This may easily be reduced to the form

$$V \begin{vmatrix} \frac{\partial \Pi}{\partial H} & \frac{\partial \Pi}{\partial V} \\ \frac{\partial T}{\partial H} & \frac{\partial T}{\partial V} \end{vmatrix},$$

which, by equation 6, is equal to zero. We have thus shown that Φ is a function of T .

Equation 3 may be written in the form

$$\begin{aligned} d\Phi &= \left[-H + V \frac{\partial \Pi}{\partial T} \right] dT \\ &= [-H + Vf'(T)] dT, \end{aligned}$$

in which $f'(T)$ denotes the derivative of the function which appears in equation 4. As Φ is a function of T , it follows that

$$-H + Vf'(T)$$

must be a function of T . To express this algebraically, it is sufficient to write

$$\begin{vmatrix} \frac{\partial}{\partial H} [-H + Vf'(T)] & \frac{\partial}{\partial V} [-H - Vf'(T)] \\ \frac{\partial T}{\partial H} & \frac{\partial T}{\partial V} \end{vmatrix} = 0.$$

On performing the indicated differentiations we get

$$\begin{vmatrix} -1 + Vf''(T) & \frac{\partial T}{\partial H} \\ f'(T) + Vf''(T) & \frac{\partial T}{\partial V} \end{vmatrix} = 0,$$

which reduces to

$$\begin{vmatrix} -1 & f'(T) \\ \frac{\partial T}{\partial H} & \frac{\partial T}{\partial V} \end{vmatrix} = 0.$$

If we expand this determinant we find that

$$f'(T) = - \frac{\left(\frac{\partial T}{\partial V} \right)_H}{\left(\frac{\partial T}{\partial H} \right)_V} \quad (8)$$

$$= - \left(\frac{\partial T}{\partial V} \right)_H \cdot \left(\frac{\partial H}{\partial T} \right)_V. \quad (9)$$

If, finally, we make use of the well-known relation

$$\left(\frac{\partial V}{\partial H} \right)_T \cdot \left(\frac{\partial H}{\partial T} \right)_V \cdot \left(\frac{\partial T}{\partial V} \right)_H = -1,$$

equation 9 takes the form of Clapeyron's equation,

$$\frac{dH}{dT} = \left(\frac{\partial H}{\partial V} \right)_T. \quad (10)$$

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