

# ON THE STABILITY OF THE EQUILIBRIUM OF UNIVARIANT SYSTEMS

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The following properties of the multiple point of an  $n$ -component system are well known:

At the temperature and under the pressure of the multiple point  $n + 2$  phases can coexist in equilibrium. At the temperature and under the pressure of the multiple point the system of  $n + 2$  phases admits of a continuous series of states of equilibrium in which the entropy and the volume of the system and the masses of the phases change, while the total thermodynamic potential of the system and the concentration of the phases remain unaltered. The state of equilibrium is completely determined if, in addition to the masses of the independent components, the volume and the entropy of the system be given.

If we represent the multiple point by a point in the temperature-pressure plane, there will pass through this point  $n + 2$  curves, each of which represents the states of equilibrium of one of the  $n + 2$  univariant systems which can be formed by suppressing one of the phases of the univariant system.

The multiple point divides each of these curves into two parts; along one of these parts the equilibrium of the corresponding univariant system is stable, while along the other part the equilibrium is unstable. The object of the present note is to establish the following two theorems which enable us to distinguish the stable from the unstable portions of the temperature-pressure curves.

I. Consider at the temperature and under the pressure of the multiple point a reversible change which increases the entropy of the invariant system, but which leaves its volume unchanged. During this change the masses of certain of the phases increase, while the masses of the others decrease. If the mass of the  $i$ -th phase increases, then the  $i$ -th univariant system,

that is to say, the univariant system in which the  $i$ -th phase is lacking, cannot exist in stable equilibrium at temperatures higher than that of the multiple point. If, on the other hand, the mass of the  $i$ -th phase diminishes, then the  $i$ -th univariant system cannot exist at temperatures lower than that of the multiple point.

II. Consider at the temperature and under the pressure of the multiple point a reversible change which diminishes the volume of the invariant system, but which leaves its entropy unchanged. During this change the masses of certain of the phases increase while the masses of the others decrease. If the mass of the  $i$ -th phase increases, then the  $i$ -th univariant system cannot exist in stable equilibrium under pressures greater than that of the multiple point. If, on the other hand, the mass of the  $i$ -th phase diminishes, then the  $i$ -th univariant system cannot exist under pressures lower than that of the multiple point.

These two theorems are for invariant systems, the analogues of the theorems of Moutier and of Robin for univariant systems. They are due to Bakhuis Roozeboom.<sup>1</sup>

To establish the first theorem, consider at the temperature and under the pressure of the multiple point the  $i$ -th univariant system in equilibrium. If we keep the volume of the system fixed we can cause the  $i$ -th phase to appear either by increasing or by decreasing the entropy of the system. Suppose that an increase of entropy causes the  $i$ -th phase to appear. Denote the total thermodynamic potential, the entropy and the volume of the system in the first state of equilibrium by  $\Phi_1$ ,  $H_1$ ,  $V_1$ , and in the second state of equilibrium by  $\Phi_2$ ,  $H_2$ ,  $V_2$ . Then we have obviously the following relations :

$$\begin{aligned}\Phi_1 &= \Phi_2, \\ H_1 &< H_2, \\ V_1 &= V_2.\end{aligned}\tag{1}$$

If we take the system in the first state of equilibrium and if, without changing the concentrations, we change the temperature

<sup>1</sup> Recueil des travaux chimiques des Pays-Bas, 6, 329 (1887). Die heterogenen Gleichgewichte, 1, 43 (1901).

T and the pressure  $\Pi$ , the change in the thermodynamic potential will be given by the equation

$$d\Phi_1 = -H_1 dT + V_1 d\Pi. \quad (2)$$

In like manner, if we take the system in the second state of equilibrium and if, without changing the concentrations, we change the temperature and the pressure, the change in the potential will be given by the equation

$$d\Phi_2 = -H_2 dT + V_2 d\Pi. \quad (3)$$

If we suppose that the change in temperature  $dT$  is positive, equations 1, 2, 3 yield immediately

$$\Phi_1 + d\Phi_1 > \Phi_2 + d\Phi_2. \quad (4)$$

If we remember that at a given temperature and under a given pressure a system cannot be in stable equilibrium unless its thermodynamic potential has the smallest value possible at that temperature and under that pressure, it follows from inequality 4 that, at a temperature slightly higher than that of the multiple point and under a pressure equal to or slightly different from that of the multiple point, the  $i$ -th univariant system cannot be in stable equilibrium. This establishes the first part of Theorem I.

Suppose that at the temperature and under the pressure of the multiple point a decrease in the entropy of the system, kept at constant volume, is necessary if the  $i$ -th phase is to appear. Equations 1 are to be replaced by the following:

$$\begin{aligned} \Phi_1 &= \Phi_2, \\ H_1 &> H_2, \\ V_1 &= V_2. \end{aligned} \quad (5)$$

If we suppose that  $dT$  is negative, equations 5, 2, 3 yield immediately inequality 4. It follows that, at a temperature slightly lower than that of the multiple point and under a pressure equal to or slightly different from that of the multiple point, the  $i$ -th univariant system cannot be in stable equilibrium. This establishes the second part of Theorem I.

Theorem II. can be established by a course of reasoning in

all respects similar to that just given. Instead of the conditions 1 and 5 we now have to consider the conditions

$$\begin{array}{ccc} \Phi_1 = \Phi_2, & & \Phi_1 = \Phi_2, \\ H_1 = H_2, & \text{and} & H_1 = H_2, \\ V_1 > V_2, & & V_1 < V_2. \end{array}$$

With the first set of conditions we take  $d\Pi$  positive, with the second set negative. In each case we obtain inequality 4.

The demonstration which we have just given is entirely analogous to the demonstration which we have given<sup>1</sup> of the theorems of Moutier and of Robin.

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<sup>1</sup> Jour. Phys. Chem. **3**, 548 (1899).