ON THE STABILITY OF THE EQUILIBRIUM OF MULTIVARIANT SYSTEMS

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The following properties of an n-component bivariant system are well-known:

At a given temperature and under a given pressure n-phases can coexist in equilibrium. At the given temperature and under the given pressure the state of equilibrium of the system is determinate, that is to say, the masses of the phases and their concentrations are determinate. There exist, however, exceptional states of the system such that, without changing the temperature or the pressure, the system can be subjected to a reversible change during which the entropy and the volume of the system and the masses of the phases change, while the concentrations of the phases and the total thermodynamic potential of the system remain constant. The state of equilibrium becomes determinate if, in addition to the masses of the components, the volume or the entropy of the system be given. These exceptional states of bivariant systems are called indifferent points.

By removing one of the n-phases of the bivariant system we can form n different trivariant systems. Each of these systems can be in equilibrium at a series of temperatures and under a series of pressures. The temperature and the pressure can be chosen independently, but then the state of equilibrium of the trivariant system is completely determined.

If, starting at the temperature and under the pressure of the indifferent point of the bivariant system, we keep the pressure of any one of the derived trivariant systems constant but vary its temperature, it will be found that the equilibrium of the trivariant system will be stable at temperatures higher than that of the indifferent point, and unstable at temperatures lower than that of the indifferent point, or else that the equilibrium will be unstable at the higher and stable at the lower temperatures.

In like manner, if we keep the temperature equal to that of the indifferent point and allow the pressure to vary, it will be found that the equilibrium of any one of the derived trivariant systems will be stable for pressures on one side of the pressure of the indifferent point and unstable for pressures on the other side of that pressure.

The following two theorems enable us to distinguish the stable from the unstable states of equilibrium of the trivariant systems.

I. Consider the bivariant system in equilibrium at an indifferent point. Without changing the temperature or the pressure of the system, let us subject it to a reversible change which increases its entropy. During this change, the mass of each phase will, in general, 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 trivariant system, that is to say, the trivariant system in which the i-th phase is lacking, cannot exist in stable equilibrium under the given pressure at temperatures higher than that of the indifferent point. If, on the contrary, the mass of the i-th phase diminishes, then the i-th trivariant system cannot exist at temperatures lower than that of the indifferent point.

II. Consider the bivariant system in equilibrium at an indifferent point. Without changing the temperature or the pressure of the system, let us subject it to a reversible change which diminishes its volume. During this change, the mass of each phase will, in general, 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 trivariant system cannot exist in stable equilibrium at the given temperature under pressures greater than that of the indifferent point. If, on the contrary, the mass of the i-th phase diminishes, then the i-th trivariant system cannot exist under pressures lower than that of the indifferent point.

To establish these theorems it is sufficient to repeat verbatim the demonstration by which we have established the corresponding theorems for the bivariant systems which can be derived from a given univariant system.[1] We consider the *i*-th trivariant system in equilibrium at an indifferent point of the original bivariant system. Without changing the temperature or the pressure we can cause the *i*-th phase to appear. This necessitates a certain change in the entropy and a corresponding change in the volume of the system. If we denote the total thermodynamic potential, the entropy and the volume of the system in the first state of equilibrium by Φ_1, H_1, V_1, and in the second state of equilibrium by Φ_2, H_2, V_2, the various conditions and equations given in the previous note become at once applicable.

For the sake of clearness we have, in the statement of the two theorems, spoken of a bivariant system and the derived trivariant systems, but it is obvious that the same theorems hold for the different systems that can be derived from a multivariant system at an indifferent point by suppressing one of its phases.

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[1] Jour. Phys. Chem. 8, 436 (1904).