

## ON THE PHASE RULE

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BY PAUL SAUREL

The very simple demonstration which Wind has given<sup>1</sup> of the phase rule is based upon a theorem which may be stated as follows: <sup>2</sup> If a system of phases is in equilibrium at a given temperature and under a given pressure, then, to each of the independent virtual changes which the system can undergo at that temperature and under that pressure, there corresponds a relation between the following variables: the concentrations of the phases, the temperature and the pressure.

As the demonstration of the phase rule follows immediately from this theorem, it may be of interest to show that this theorem may be regarded as one way of stating the conditions of equilibrium which we have given in a previous paper.<sup>3</sup>

Consider a system of  $r$  phases formed by means of  $n$  independent components. Denote by  $M_{ij}$  the mass of the  $j$ -th component which appears in the  $i$ -th phase; there will be  $nr$  such quantities. To determine the number of independent virtual changes of which the system is capable at the given temperature under the given pressure and with the given masses of the independent components, we must determine how many of the masses  $M_{ij}$  are independently variable.

In the first place, the variations of the masses  $M_{ij}$  are subject to the conditions that the total mass of each component in the system remain invariable; these conditions are expressed by the  $n$  equations

$$\sum_{i=1}^r \delta M_{ij} = 0, \quad j = 1, 2, \dots, n. \quad (1)$$

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<sup>1</sup> Zeit. phys. Chem. **31**, 390 (1899).

<sup>2</sup> Zeit. phys. Chem. **31**, 391 (1899).

<sup>3</sup> Jour. Phys. Chem. **5**, 31 (1901).

Moreover, it may happen that certain of the components cannot enter into certain of the phases. We thus have a certain number of equations of the form

$$\delta M_{ij} = 0. \quad (2)$$

We shall suppose that there are  $p$  equations of this form. Finally, it may happen that certain of the components can enter certain of the phases only when associated with other components in definite proportions. Accordingly there will be a certain number of conditions of the form

$$\delta M_{ij} = \lambda \delta M_{ik}, \quad (3)$$

in which  $\lambda$  is a constant. We shall suppose that there are  $q$  conditions of this form. The system accordingly admits of only  $nr - n - p - q$  independent virtual changes.

Denote by  $m_{ij}$  the mass of the  $j$ -th component which appears in the unit of mass of the  $i$ -th phase. This quantity may be called the concentration of the  $j$ -th component in the  $i$ -th phase. In the paper referred to above we have shown<sup>1</sup> that the conditions of equilibrium of the system are expressed by the equations

$$F_{1j} = F_{2j} = \dots = F_{rj}, \quad j = 1, 2, \dots, n, \quad (4)$$

in which the functions  $F_{ij}$  are functions of the temperature, the pressure and the  $nr$  concentrations. The above equations apparently furnish  $n(r - 1)$  equations between these  $nr + 2$  variables. But in the demonstration by which these equations were established it was shown that  $p$  of the functions  $F_{ij}$  corresponding to the  $p$  equations 2 are identically equal to zero and are to be omitted from equations 4. Moreover,  $q$  of the equations 4 corresponding to the  $q$  conditions 3 are mere identities and do not furnish relations between the variables. The conditions of equilibrium 4 thus furnish  $nr - n - p - q$  relations between the temperature, the pressure and the concentrations. We have thus established the theorem that the number of equations 4 is the same as the number of independent virtual changes of the system. Moreover, by referring to the demonstration by means

<sup>1</sup> Jour. Phys. Chem. 5, 31 (1901).

of which equations 4 are established, it is not difficult to see that to each of the independent virtual changes there may be made to correspond one of the equations of equilibrium.

The phase rule follows immediately from equations 4. For, from the definition of the concentrations and the definition of the system, it follows that the  $nr$  concentrations are not independent, but are subject to the  $r$  conditions

$$\sum_{j=1}^n m_{ij} = 1, \quad i = 1, 2, \dots, r, \quad (5)$$

to  $p$  equations to the form

$$m_{ij} = 0, \quad (6)$$

corresponding to the  $p$  equations 2, and to  $q$  equations of the form

$$m_{ij} = \lambda m_{ik}, \quad (7)$$

corresponding to the  $q$  equations 3. Thus, from the definition of the system, the temperature, the pressure and the concentrations are subject to  $r + p + q$  conditions; from the conditions of equilibrium 4 these variables are subject to  $nr - n - p - q$  additional conditions. There are thus  $nr - n + r$  conditions among the  $nr + 2$  variables in question; in other words, only  $n + 2 - r$  of these variables are independent.

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