"Sur le déplacement de l'éequilibre," Ann. Sci. de la É. N. S (3) 9 (1892), 375-379.

## ON THE

## **DISPLACEMENT OF EQUILIBRIUM**

## By P. DUHEM

Translated by D. H. Delphenich

The law of displacement of equilibrium with temperature was stated in 1884 by J.-H. Van t'Hoff. The law of displacement of equilibrium with pressure was then stated in the same year by H. Le Chatelier. I have given those two laws a proof that is based upon the principles of thermodynamics (<sup>1</sup>) Today, I propose to state and prove a generalization of the second one.

Imagine a system that is defined by its absolute temperature *T* and a certain number of independent parameters  $\alpha$ ,  $\beta$ , ...,  $\lambda$ . The system is subject to certain external forces. Under a virtual isothermal modification that makes the parameters  $\alpha$ ,  $\beta$ , ...,  $\lambda$  submit to variations  $\delta \alpha$ ,  $\delta \beta$ , ...,  $\delta \lambda$ , those forces will do an amount of work equal to:

$$dT_e = A \,\,\delta\alpha + B \,\,\delta\beta + \ldots + L \,\,\delta\lambda$$

Under the action of forces A, B, ..., L, the system will take on an equilibrium state that is defined by the values of  $\alpha, \beta, ..., \lambda$  of the independent parameters, when the temperature T is supposed to have been given. Those values of  $\alpha, \beta, ..., \lambda$  that correspond to equilibrium are determined in the following manner:

Let  $\mathcal{F}(\alpha, \beta, ..., \lambda, T)$  be the internal thermodynamics potential of the system. In the equilibrium state, we will have:

(1)  
$$\begin{cases} \frac{\partial \mathcal{F}}{\partial \alpha} = A, \\ \frac{\partial \mathcal{F}}{\partial \beta} = B, \\ \dots, \\ \frac{\partial \mathcal{F}}{\partial \lambda} = L. \end{cases}$$

<sup>(&</sup>lt;sup>1</sup>) P. DUHEM, "Sur le déplacement de l'équilibre, Ann. de la Fac. Sci. de Toulouse, t. IV, N.

When those equations (1) are solved for  $\alpha$ ,  $\beta$ , ...,  $\lambda$ , that will give the values of those parameters that correspond to equilibrium.

Let the temperature have the value *T* and give new values to the external forces A + dA, B + dB, ..., L + dL. The system will take on a new equilibrium state that is defined by the values  $\alpha + d\alpha$ ,  $\beta + d\beta$ , ...,  $\lambda + d\lambda$  of the parameters  $\alpha$ ,  $\beta$ , ...,  $\lambda$ .

When the equalities (1) are differentiated, they will give:

$$\frac{\partial^{2} \mathcal{F}}{\partial \alpha^{2}} d\alpha + \frac{\partial^{2} \mathcal{F}}{\partial \alpha \partial \beta} d\beta + \dots + \frac{\partial^{2} \mathcal{F}}{\partial \alpha \partial \lambda} d\lambda = dA,$$

$$\frac{\partial^{2} \mathcal{F}}{\partial \beta \partial \alpha} d\alpha + \frac{\partial^{2} \mathcal{F}}{\partial \beta^{2}} d\beta + \dots + \frac{\partial^{2} \mathcal{F}}{\partial \beta \partial \lambda} d\lambda = dB,$$

$$\dots$$

$$\frac{\partial^{2} \mathcal{F}}{\partial \lambda \partial \alpha} d\alpha + \frac{\partial^{2} \mathcal{F}}{\partial \lambda \partial \beta} d\beta + \dots + \frac{\partial^{2} \mathcal{F}}{\partial \lambda^{2}} d\lambda = dL.$$

Multiply the first of those equalities by  $d\alpha$ , the second one by  $d\beta$ , ..., and the last one by  $d\lambda$ , and add corresponding sides of the resulting equations that one obtains. One will find that:

(2) 
$$\begin{cases} \frac{\partial^2 \mathcal{F}}{\partial \alpha^2} (d\alpha)^2 + \frac{\partial^2 \mathcal{F}}{\partial \beta^2} (d\beta)^2 + \dots + \frac{\partial^2 \mathcal{F}}{\partial \lambda^2} (d\lambda)^2 + 2\sum \frac{\partial^2 \mathcal{F}}{\partial \mu \partial \nu} d\mu d\nu \\ = dA d\alpha + dB d\beta + \dots + dL d\lambda. \end{cases}$$

In that equation, one must attribute the following significance to the symbol:

$$\sum \frac{\partial^2 \mathcal{F}}{\partial \mu \partial \nu} \, d\mu \, d\nu :$$

One considers all values of the quantity:

$$\frac{\partial^2 \mathcal{F}}{\partial \mu \partial v} \, d\mu dv$$

that are distinct from each other and can be obtained by replacing  $\mu$  and  $\nu$  with two distinct letters that are taken from the set  $\alpha$ ,  $\beta$ , ...,  $\lambda$ , and one then takes the sum over all distinct values.

We propose to determine the sign of the left-hand side of equation (2).

When subjected to *constant* forces *A*, *B*, ..., *L*, the system will admit a total thermodynamic potential:

$$\Phi(\alpha, \beta, ..., \lambda, T) = F(\alpha, \beta, ..., \lambda, T) - (A \alpha + B \beta + ... + L \lambda).$$

If one leaves the temperature constants and subjects the variables  $\alpha$ ,  $\beta$ , ...,  $\lambda$  to arbitrary increases  $\delta \alpha$ ,  $\delta \beta$ , ...,  $\delta \lambda$  then that potential will experience an increase:

(3)  

$$\begin{cases}
\delta \Phi(\alpha, \beta, ..., \lambda, T) \\
= \left(\frac{\partial \mathcal{F}}{\partial \alpha} - A\right) \delta \alpha + \left(\frac{\partial \mathcal{F}}{\partial \beta} - B\right) \delta \beta + \dots + \left(\frac{\partial \mathcal{F}}{\partial \lambda} - L\right) \delta \lambda \\
+ \frac{\partial^2 \mathcal{F}}{\partial \alpha^2} (\delta \alpha)^2 + \frac{\partial^2 \mathcal{F}}{\partial \beta^2} (\delta \beta)^2 + \dots + \frac{\partial^2 \mathcal{F}}{\partial \lambda^2} (\delta \lambda)^2 + 2\sum \frac{\partial^2 \mathcal{F}}{\partial \mu \partial \nu} \delta \mu \delta \nu
\end{cases}$$

In order for the system to be in *stable* equilibrium under the action of constant forces A, B, ..., L, it will suffice that  $\Phi$  should be a minimum.

In order for  $\Phi$  to be a minimum, it is necessary and sufficient that:

1. The set of terms of first degree in  $\delta \alpha$ ,  $\delta \beta$ , ...,  $\delta \lambda$  on the right-hand side of the equality (3) must be equal to zero, which will reproduce the equalities (1).

2. The set of second-degree terms must be essentially positive.

The quantity:

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$$\frac{\partial^2 \mathcal{F}}{\partial \alpha^2} (\delta \alpha)^2 + \frac{\partial^2 \mathcal{F}}{\partial \beta^2} (\delta \beta)^2 + \dots + \frac{\partial^2 \mathcal{F}}{\partial \lambda^2} (\delta \lambda)^2 + 2 \sum \frac{\partial^2 \mathcal{F}}{\partial \mu \partial \nu} \, \delta \mu \, \delta \nu$$

will then be positive, no matter what values are taken by the quantities  $\delta \alpha$ ,  $\delta \beta$ , ...,  $\delta \lambda$ , provided that those values are not all equal to 0. In particular, that quantity will be positive if one sets:

$$\delta \alpha = d\alpha, \ \delta \beta = d\beta, \dots, \delta \lambda = d\lambda.$$

The equality (2) will then show that one has:

(4) 
$$dA \ d\alpha + dB \ d\beta + \ldots + dL \ d\lambda > 0 .$$

That inequality expresses the general theorem to which we would like to arrive, and which can be stated thus:

A system is in stable equilibrium at a given temperature under the action of certain external forces. One then adds new infinitely-small forces to those external forces, while the temperature remains the same. The original equilibrium is perturbed, and a new state of equilibrium is established. The work done by the perturbing forces during the transition from the old equilibrium state to the new one is always positive.

It is easy to see that this general theorem includes the proposition of H. le Chatelier as a special case:

Imagine that a system is in equilibrium under the action of an external pressure that is normal and uniform. Give an infinitely-small increase to that pressure. The original equilibrium is perturbed, and a new equilibrium state is established. Under the passage from the old equilibrium state to the new one, the additional pressure must do positive work. That passage will then be accompanied by a reduction in volume.

The preceding theorem takes an interesting form in the case that one frequently encounters in the study of elasticity, in which original equilibrium state is the *natural state*, i.e., the state in which the body is devoid of any external force. That will then imply the following proposition:

## When the forces imprint an arbitrary deformation on an elastic body when one starts from a natural state that is supposed to be stable, the work done by those forces must certainly be positive.

In a previous note, I treated a problem that relates to the deformation of crystals (<sup>1</sup>), which is a problem that has some interesting relationships to the theory of displacement of equilibrium. The developments that I discussed rest upon the use of certain equalities that were given in my *Leçons* sur l'Électricité et le Magnétisme [t. II, pp. 472, equalities (12)]. Now, those equalities are affected with a sign error, as one will easily recognize upon comparing the equalities with the ones from which they are deduced [*loc. cit.*, pp. 471, equalities (11)]. The results that I obtained must then *have their signs changed*, which will make the disagreement that they present with those of Lippmann and Pockels disappear. I would like to thank F. Pockels for having been kind enough to point out that inexactitude to me.

<sup>(&</sup>lt;sup>1</sup>) Ann. de l'É. N. S (3), t. IX, pp. 167.