"Sur le déplacement de l'équilibre," Ann. fac. sci. Toulouse (1) 4 (1890), N1-N9.

On the displacement of equilibrium

By P. DUHEM

Lecturer in a complementary course with the Faculté des Sciences de Lille

Translated by D. H. Delphenich

1.

The application of thermodynamics to chemical mechanics has transformed the ideas of physicists that touch upon the influence that heat has on chemical combinations. The main result to which it leads can be summarized in a very simple principle.

The invention of this beautiful theorem must be attributed to J. Moutier, although that physicist stated it for only decompositions within perfectly-heterogeneous systems that are similar to the one that is composed of calcium carbonate, calcium, and carbonic acid, which is a system in which equilibrium is determined by a dissociation pressure (*tension de dissociation*) that is a function of only temperature.

In 1877 (¹), by considering a very simple cycle and applying Clausius's theorem to that cycle, Moutier arrived at the following theorem:

When a transformation is accomplished under a well-defined pressure, there exists only one temperature for which the transformation is reversible. Below that temperature, the transformation will always take place that will produce a release of heat. Above that temperature, the transformation will always take place that is accomplished by an absorption of heat.

A little later (²), Moutier showed the importance of that proposition in the domain of chemical mechanics.

In 1882, J.-H. Van t'Hoff (³) stated that proposition in an absolutely general form for any type of chemical transformation. That fertile proposition, to which Van t'Hoff gave the name of the *principal of the displacement material equilibrium with temperature*, was stated by him in the following manner:

^{(&}lt;sup>1</sup>) J. MOUTIER, "Sur les transformations non reversible," Société philomathique (7) **1** (1877), pp. 39.

 ^{(&}lt;sup>2</sup>) J. MOUTIER, "Sur les combinaisons chimiques produites avec absorption de chaleur," Société philomathique
 (7) 1 (1877), pp. 96.

^{(&}lt;sup>3</sup>) J.-H. VAN T'HOFF, Études de Dynamique chimique, Amsterdam, 1884, pp. 161.

Any equilibrium between two different states of matter (systems) will displace towards the system whose formation develops heat under a reduction of temperature.

In 1886, Potier $(^1)$ gave a proof of that proposition.

During the school year 1888-1889, we taught the laws of chemical mechanics while on the science faculty at Lille. In the course of teaching that subject, we gave the following proof of J.-H. Van t'Hoff's proposition:

Imagine a system that is defined by absolute temperature *T* and a certain number of other parameters α , β , ..., λ . Suppose that the external forces that are applied to that system admit a potential *W*, either by themselves or by virtue of the constraints that are imposed upon the virtual modifications that one affects the system with.

The system thus-constituted will admit a thermodynamic potential Φ .

The equilibrium conditions for the system at the temperature T will be represented by the equations:

(1)
$$\begin{cases} \frac{\partial \Phi}{\partial \alpha} = 0, \\ \frac{\partial \Phi}{\partial \beta} = 0, \\ \frac{\partial \Phi}{\partial \lambda} = 0. \end{cases}$$

When solved for α , β , ..., λ , those equations will become:

(2)
$$\begin{cases} \alpha = \alpha(T), \\ \beta = \beta(T), \\ \dots, \\ \lambda = \lambda(T). \end{cases}$$

The latter equations define the state of the system at the temperature T.

At the temperature (T + dT), a new equilibrium state is established in which the parameters that define the system will have the new values:

$$lpha + rac{dlpha}{dT}dT$$
,
 $eta + rac{deta}{dT}dT$,
.....

^{(&}lt;sup>1</sup>) POTIER, J. de Phys. (2) **5** (1886).

$$\lambda + \frac{d\lambda}{dT}dT$$

When the equations of equilibrium (1) are differentiated with respect to T, they will give the system of equations:

$$\frac{\partial^2 \Phi}{\partial \alpha \partial T} + \frac{\partial^2 \Phi}{\partial \alpha^2} \frac{d\alpha}{dT} + \frac{\partial^2 \Phi}{\partial \alpha \partial \beta} \frac{d\beta}{dT} + \dots + \frac{\partial^2 \Phi}{\partial \alpha \partial \lambda} \frac{d\lambda}{dT} = 0,$$

$$\frac{\partial^2 \Phi}{\partial \beta \partial T} + \frac{\partial^2 \Phi}{\partial \beta \partial \alpha} \frac{d\alpha}{dT} + \frac{\partial^2 \Phi}{\partial \beta^2} \frac{d\beta}{dT} + \dots + \frac{\partial^2 \Phi}{\partial \beta \partial \lambda} \frac{d\lambda}{dT} = 0,$$

$$\dots$$

$$\frac{\partial^2 \Phi}{\partial \lambda \partial T} + \frac{\partial^2 \Phi}{\partial \lambda \partial \alpha} \frac{d\alpha}{dT} + \frac{\partial^2 \Phi}{\partial \lambda \partial \beta} \frac{d\beta}{dT} + \dots + \frac{\partial^2 \Phi}{\partial \lambda^2} \frac{d\lambda}{dT} = 0.$$

We multiply the two sides of the first of those equations by $d\alpha / dT$, both sides of the second one by $d\beta / dT$, ..., both sides of the last one by $d\lambda / dT$ and then add corresponding sides of the results obtained. We will then get the following result:

(3)
$$\begin{cases} \frac{\partial^2 \Phi}{\partial \alpha \,\partial T} \frac{d\alpha}{dT} + \frac{\partial^2 \Phi}{\partial \beta \,\partial T} \frac{d\beta}{dT} + \dots + \frac{\partial^2 \Phi}{\partial \lambda \,\partial T} \frac{d\lambda}{dT} \\ + \frac{\partial^2 \Phi}{\partial \alpha^2} \left(\frac{d\alpha}{dT}\right)^2 + \frac{\partial^2 \Phi}{\partial \beta^2} \left(\frac{d\beta}{dT}\right)^2 + \dots + \frac{\partial^2 \Phi}{\partial \lambda^2} \left(\frac{d\lambda}{dT}\right)^2 + 2\sum \frac{\partial^2 \Phi}{\partial \mu \,\partial \nu} \frac{d\mu}{dT} \frac{d\nu}{dT} = 0 \end{cases}$$

In that equation, the symbol:

$$\sum \frac{\partial^2 \Phi}{\partial \mu \partial \nu} \frac{d\mu}{dT} \frac{d\nu}{dT}$$

must be given the following significance:

One considers all of the mutually-distinct values of the quantity:

$$\frac{\partial^2 \Phi}{\partial \mu \partial \nu} \frac{d\mu}{dT} \frac{d\nu}{dT}$$

that one can obtain by replacing μ with ν with two letters that are different from each other and are taken from the set α , β , ..., λ , and one then takes the sum of all those distinct values.

By hypothesis, the equalities (2) define the equilibrium state of the system at the temperature *T*. They then make the thermodynamic potential Φ a minimum. Moreover, if one gives the values to α , β , ..., λ that are defined by the equalities (2) then one will know that the quadratic form:

$$\frac{\partial^2 \Phi}{\partial \alpha^2} a^2 + \frac{\partial^2 \Phi}{\partial \beta^2} a^2 + \dots + \frac{\partial^2 \Phi}{\partial \lambda^2} l^2 + 2\sum \frac{\partial^2 \Phi}{\partial \mu \partial \nu} mn$$

must be positive for any of those non-zero values that gives to the quantities a, b, ..., l.

In particular, that must be true if one sets:

$$a = \frac{d\alpha}{dT}$$
, $b = \frac{d\beta}{dT}$, ..., $l = \frac{d\lambda}{dT}$.

One then has:

$$\frac{\partial^2 \Phi}{\partial \alpha^2} \left(\frac{d\alpha}{dT} \right)^2 + \frac{\partial^2 \Phi}{\partial \beta^2} \left(\frac{d\beta}{dT} \right)^2 + \dots + \frac{\partial^2 \Phi}{\partial \lambda^2} \left(\frac{d\lambda}{dT} \right)^2 + 2\sum \frac{\partial^2 \Phi}{\partial \mu \partial \nu} \frac{d\mu}{dT} \frac{d\nu}{dT} > 0.$$

When that inequality is compared to the equality (3), that will give the inequality:

$$\frac{\partial^2 \Phi}{\partial \alpha \,\partial T} \frac{d\alpha}{dT} + \frac{\partial^2 \Phi}{\partial \beta \,\partial T} \frac{d\beta}{dT} + \dots + \frac{\partial^2 \Phi}{\partial \lambda \,\partial T} \frac{d\lambda}{dT} < 0.$$

Set:

(4)
$$\delta \alpha = \frac{d\alpha}{dT} dT, \qquad \delta \beta = \frac{d\beta}{dT} dT, \dots, \qquad \delta \lambda = \frac{d\lambda}{dT} dT.$$

The inequality that we just obtained can be stated in the following manner:

The quantity:

$$\frac{\partial^2 \Phi}{\partial \alpha \,\partial T} \,\,\delta \alpha + \frac{\partial^2 \Phi}{\partial \beta \,\partial T} \,\,\delta \beta + \dots + \frac{\partial^2 \Phi}{\partial \lambda \,\partial T} \,\,\delta \lambda$$

has the opposite sign to dT.

Let us interpret that result:

When a system is subjected to a real or virtual modification at a constant temperature T, it will release a quantity of heat dQ. It will result from the expression for the thermodynamic potential itself that:

$$E dQ + d\sum \frac{mv^2}{2} = -d\left(\Phi - T\frac{\partial\Phi}{\partial T}\right).$$

In particular if the modification starts from an equilibrium state then one will have:

$$d\sum \frac{mv^2}{2} = 0,$$
$$d\Phi = 0,$$

and the preceding equality will become:

$$E\,dQ = T\,d\,\frac{\partial\Phi}{\partial T}\,.$$

We then take the system under study in its equilibrium state at the temperature *T*. We give virtual variations to the parameters α , β , ..., λ that characterize it that are equal to the quantities $\delta \alpha$, $\delta \beta$, ..., $\delta \lambda$ that are defined by the equalities (4), and we keep the temperature invariable. The system will release a quantity of heat δQ that is expressed by the relation:

$$\delta Q = \frac{T}{E} \left(\frac{\partial^2 \Phi}{\partial \alpha \, \partial T} \, \delta \alpha + \frac{\partial^2 \Phi}{\partial \beta \, \partial T} \, \delta \beta + \dots + \frac{\partial^2 \Phi}{\partial \lambda \, \partial T} \, \delta \lambda \right) \, .$$

From what we have seen, the right-hand side of that equality has the opposite sign to dT; we can then state the following theorem:

When one raises the temperature of a system in equilibrium, it will establish a new equilibrium state that is different from the first one. The parameters that characterize the state of the system will submit to certain variations. If they had suffered those same variations while the temperature remained constant then the modification that was imposed upon the system would imply a release of heat.

One can see that this is the general principle that J.-H. Van t'Hoff asserted.

II.

In 1882, G. Robin (¹) showed that the method that was employed by J. Moutier to prove the proposition that we stated at the beginning of this article easily extends to the proof of the following proposition:

At a certain well-defined temperature, there exists only one pressure at which equilibrium is established. At higher pressures, a reaction will be produced that is accompanied by a reduction of volume. At lower pressures, a reaction will be produced that is accompanied by an increase in volume.

Robin stated that theorem for only the case of perfectly-heterogeneous systems. However, like the preceding statement, it is capable of being extended to arbitrary systems. Let us prove it in a general manner.

Consider a system that is subject to a normal and uniform pressure P that is the only external force that acts upon it. Let V be its volume. Let U and S be its internal energy and entropy. Let:

^{(&}lt;sup>1</sup>) G. Robin, Société mathématique (7) **4** (1882), pp. 24.

$$\Phi = E \left(U - TS \right) + PV$$

be its thermodynamic potential under constant pressure *P*. Suppose that the state of the system is defined by the variables *P*, *T*, α , β , ..., λ . The equilibrium conditions for the system under a pressure *P* and at a temperature *T* are:

(5)
$$\begin{cases} \frac{\partial \Phi}{\partial \alpha} = 0, \\ \frac{\partial \Phi}{\partial \beta} = 0, \\ \frac{\partial \Phi}{\partial \lambda} = 0, \\ \frac{\partial \Phi}{\partial \lambda} = 0, \end{cases}$$

which are equations that will become:

(6)
$$\begin{cases} \alpha = \alpha(P,T), \\ \beta = \beta(P,T), \\ \dots \\ \lambda = \lambda(P,T), \end{cases}$$

when they are solved for α , β , ..., λ .

Exert a pressure (P + dP) on the system at the same temperature *T*. A new state of equilibrium will be established. The variables α , β , ..., λ must take the new values:

$$\alpha(P, T) + \frac{\partial \alpha(P, T)}{\partial P} dP,$$

$$\beta(P, T) + \frac{\partial \beta(P, T)}{\partial P} dP,$$

....,

$$\lambda(P, T) + \frac{\partial \lambda(P, T)}{\partial P} dP.$$

Differentiate the equilibrium conditions (5) with respect to *P*. That will give the following equalities:

$$\frac{\partial^2 \Phi}{\partial \alpha \,\partial P} + \frac{\partial^2 \Phi}{\partial \alpha^2} \frac{\partial \alpha}{\partial P} + \frac{\partial^2 \Phi}{\partial \beta^2} \frac{\partial \beta}{\partial P} + \dots + \frac{\partial^2 \Phi}{\partial \alpha \,\partial \lambda} \frac{\partial \lambda}{\partial P} = 0,$$

$$\frac{\partial^2 \Phi}{\partial \beta \,\partial P} + \frac{\partial^2 \Phi}{\partial \beta^2} \frac{\partial \alpha}{\partial P} + \frac{\partial^2 \Phi}{\partial \beta^2} \frac{\partial \beta}{\partial P} + \dots + \frac{\partial^2 \Phi}{\partial \beta \,\partial \lambda} \frac{\partial \lambda}{\partial P} = 0,$$

$$\dots$$

$$\frac{\partial^2 \Phi}{\partial \lambda \,\partial P} + \frac{\partial^2 \Phi}{\partial \lambda^2} \frac{\partial \alpha}{\partial P} + \frac{\partial^2 \Phi}{\partial \lambda^2} \frac{\partial \beta}{\partial P} + \dots + \frac{\partial^2 \Phi}{\partial \lambda^2} \frac{\partial \lambda}{\partial P} = 0.$$

We multiply the two sides of the first of those equations by $\frac{\partial \alpha}{\partial P}$, the two sides of the second by $\frac{\partial \beta}{\partial P}$, ..., and the two sides of the last one by $\frac{\partial \lambda}{\partial P}$, and add corresponding sides of the results obtained. We will then find the equality:

(7)
$$\begin{cases} \frac{\partial^2 \Phi}{\partial \alpha \partial P} \frac{\partial \alpha}{\partial P} + \frac{\partial^2 \Phi}{\partial \beta \partial P} \frac{\partial \beta}{\partial P} + \dots + \frac{\partial^2 \Phi}{\partial \lambda \partial P} \frac{\partial \lambda}{\partial P} \\ + \frac{\partial^2 \Phi}{\partial \alpha^2} \left(\frac{\partial \alpha}{\partial P}\right)^2 + \frac{\partial^2 \Phi}{\partial \beta^2} \left(\frac{\partial \beta}{\partial P}\right)^2 + \dots + \frac{\partial^2 \Phi}{\partial \lambda^2} \left(\frac{\partial \lambda}{\partial P}\right)^2 + 2\sum \frac{\partial^2 \Phi}{\partial \mu \partial \nu} \frac{\partial \mu}{\partial P} \frac{\partial \nu}{\partial P} = 0. \end{cases}$$

The equilibrium state of the system that is defined by the equalities (6) is such that the corresponding value of Φ is a minimum compared to all of the ones that correspond to the same values of *P* and *T*. The quadratic form:

$$\frac{\partial^2 \Phi}{\partial \alpha^2} a^2 + \frac{\partial^2 \Phi}{\partial \beta^2} b^2 + \dots + \frac{\partial^2 \Phi}{\partial \lambda^2} l^2 + 2\sum \frac{\partial^2 \Phi}{\partial \mu \partial \nu} mn$$

is then positive for any system of non-zero values for a, b, ..., l. In particular, one will have:

$$\frac{\partial^2 \Phi}{\partial \alpha^2} \left(\frac{\partial \alpha}{\partial P} \right)^2 + \frac{\partial^2 \Phi}{\partial \beta^2} \left(\frac{\partial \beta}{\partial P} \right)^2 + \dots + \frac{\partial^2 \Phi}{\partial \lambda^2} \left(\frac{\partial \lambda}{\partial P} \right)^2 + 2 \sum \frac{\partial^2 \Phi}{\partial \mu \partial \nu} \frac{\partial \mu}{\partial P} \frac{\partial \nu}{\partial P} > 0.$$

That inequality, when combined with the equality (7), will give the inequality:

$$\frac{\partial^2 \Phi}{\partial \alpha \, \partial P} \frac{\partial \alpha}{\partial P} + \frac{\partial^2 \Phi}{\partial \beta \, \partial P} \frac{\partial \beta}{\partial P} + \dots + \frac{\partial^2 \Phi}{\partial \lambda \, \partial P} \frac{\partial \lambda}{\partial P} > 0.$$

Set:

$$\delta \alpha = \frac{\partial \alpha}{\partial P} dP$$
, $\delta \beta = \frac{\partial \beta}{\partial P} dP$, ..., $\delta \lambda = \frac{\partial \lambda}{\partial P} dP$.

Observe, moreover, that from the principles of the theory of the thermodynamic potential, one has:

$$V=\frac{\partial\Phi}{\partial P}\,,$$

and the result that we just obtained can then be stated:

The quantity:

$$\frac{\partial V}{\partial \alpha} \delta \alpha + \frac{\partial V}{\partial \beta} \delta \beta + \dots + \frac{\partial V}{\partial \lambda} \delta \lambda$$

has the opposite sign to dP. Now that quantity is the variation δV that the volume will experience when the parameters α , β , ..., λ submit to the variations $\delta \alpha$, $\delta \beta$, ..., $\delta \lambda$ while the pressure P and temperature T are kept constant. One will then arrive at the following proposition:

When one increases the pressure that keeps a system in equilibrium at constant temperature, a new equilibrium state will be established that is different from the first. The parameters that characterize the state of the system submit to a certain variation. If they submit to the same variation at constant temperature while the original pressure is kept constant then there will be a reduction of volume of the system.

That proposition, which was given by G. Robin in 1882 for a special case, was stated in its general form, without proof, in 1884 by H. Le Châtelier (¹). Le Châtelier gave that proposition as a complement to the proposition of J.-H. Van t'Hoff and then presented it in the following form:

Any system in stable chemical equilibrium that is subjected to the influence of an external cause that tends to vary either its temperature, its condensation (e.g., pressure, concentration, number of molecules per unit volume), either wholly or in some of its parts, can undergo only internal modifications that would bring about a change in temperature or condensation with the opposite sign to the one that results from the external cause if they alone are produced.

With that statement, as one sees, Le Châtelier applied that theorem to not only the pressure of solutions, but also their concentrations, in the case where that parameter applies. The theorem in question can indeed be given a completely-general statement that transcends simple chemical mechanics and was given by F. Braun (²) in the following form:

When one makes a system pass from one equilibrium state to another one by modifying the values of one of the values that it depends upon, "the passage to the new equilibrium state always takes place in such a way that the arbitrary variation that is imposed on one of the variables to determine the modification will experience a reduction in its absolute value as a result of that modification."

Braun gave a proof of that proposition that was based upon only the concept of stability. One can easily give a proof of it that is based upon thermodynamics and was analogous to the one that we just gave for the case in which the variable parameter was pressure.

^{(&}lt;sup>1</sup>) H. LE CHATELIER, C. R. Acad. Sci. Paris **99** (1884), pp. 788.

^{(&}lt;sup>2</sup>) F. BRAUN, "Ueber einen allgemeinen qualitativen Satz für Zustandsänderungen nebst einigen sich anschliessenden Bemerkungen, insbesondere über nicht eindeutige Systeme," Wied. Ann. **33** (1888), pp. 337.