The laws of displacement of equilibrium and Le Chatelier's principle (¹)

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1. – The laws of displacement of equilibrium are consequences of Carnot's principle. One can express them by mathematical formulas. The use of ordinary language, which has contributed greatly to the popularization of those laws, runs the risk of not always presenting enough clarity or absolute precision. With a student who ignores the proofs, one is obliged to comment upon the terms in its statement whose significance will appear neatly only in the examples.

We shall avoid those pitfalls by developing the opposite exposition. We shall point out certain lesser-known peculiarities of the transformations, and in order to state the laws, it will suffice to confirm the generality of those peculiarities. Since we will suppress any obscurity from the outset, we will likewise have the advantage (as we will see) of making some of the ideas that relate to the question as precise as the ones that can result from a thermodynamic study.

That will permit us to recognize, in particular, that Le Chatelier's principle, as a perfectly complete and correct expression of the laws of the displacement of equilibrium, is not, at the same time, the only indispensable form that it can take. There exist other equivalent forms, although they seem quite different from the outset.

Therefore, we shall discover the laws of displacement of equilibrium by an examination of well-known properties, confirm what is essential in the facts, and find various expressions for those laws. That is the plan of the present article, in which I shall solely assume the elementary, and I hope, pedagogical viewpoint.

We shall distinguish two cases of equilibrium: Transformations at constant temperature $(^2)$, while the volume and (in general) pressure vary, transformations at constant pressure with exchanges of heat and (in general) variations in temperature.

2. Constant temperature. – Let us examine the isotherms of a *fluid* that presents a well-defined *vapor pressure*, and we suppose that the isotherm is traced in the *pv*-plane as *ABbCcD* (Fig. 1).

^{(&}lt;sup>1</sup>) Communicated to the Société française de Physique at the session on 19 March 1909.

^{(&}lt;sup>2</sup>) We intend the term "transformation" to mean any passage from an arbitrary state to another.



Figure 1.

First remark. – If one starts, for example, with a compressed liquid at A and one progressively increases the volume that is present then one will arrive at a point B where *the isotherm is bifurcated*. Upon continuing to increase the volume, one might realize two series of states at constant temperature, one of which is *stable* and heterogeneous along BC, while the other one is *less stable* and homogeneous at Bb, which consists of a liquid that is subject to a pressure that is lower than the maximum pressure.

One will have the same bifurcation when one displaces by starting from D and going beyond C.

Second remark. – On the bifurcation and difference in stability between the two paths that are equivalent in that sense: It is possible to pass from a stable state B to a likewise-stable state along BC in two ways, namely, by either a succession of stables states along BC or *in two steps*, first, by a transformation Bb that is less stable and then by an irreversible transformation. The same thing will be true when one starts from C.

Third remark. – The notation of a transformation in two steps can be extended to any point M of BC that one considers to be a starting point.

M is the symbol for a point of a system that consists of masses of vapor and liquid that are proportional to *MB* and *MC*, respectively. Upon starting from *M*, one can imagine a transformation that, like *Bb* and *Cc*, is not accompanied by any change of state. In order to do that, it would suffice to separate the two fluids and subject them to the same isothermal variation of pressure (¹), i.e., to take the unit of mass of each of the two states to be represented by two points of the isotherm that are located along a parallel to the *v*-axis. The symbolic point of the system divides the segment of that parallel that is found between *Ab* and *cD* in the ratio *MC / MB*. Its locus will be the two parts *Mm*, *Mm'* of the same curve. One can return to a point of *BC* from each of the points of *mm'*, or even from *AB* and *CD*, by an irreversible isothermal path.

^{(&}lt;sup>1</sup>) For example, by introducing a free piston between the liquid and the vapor that is contained in the same pump body such that the piston separates the fluids and transmits the pressures.

In summary: An isothermal transformation that goes from one stable state to a likewise-stable state by varying the masses of the liquid and vapor can always be replaced with a two-step transformation such that one artificially exhibits any *internal modification* during the first step.

Let us now examine two special cases of the second step:

a) The second step is at constant *volume mP*.

It is obvious that in this second step them variation of the pressure *mP* has the *opposite sign* to that of the variation in the first step *Mm*. That is Le Chatelier's principle: Any system in stable equilibrium that is subject to the action of an external cause that tends $(^1)$ to vary its pressure (at constant temperature) can produce $(^2)$ only internal modifications, and if they are the only ones that are produced $(^3)$ then they will bring about a change in pressure with the opposite sign to the one that results from the external cause (original statement, 1884).

We shall also write this by attributing the indices 1 and 2 to the two steps:

(I)
$$(T = \text{const.}, dv_2 = 0)$$
 $dp_1 dp_2 < 0$

b) The second step is at constant *pressure* m'D.

Here, the special properties of univariant systems imply the consequence that an infinitelysmall variation of volume or pressure during the first step will determine a finite variation v_2 during the second step. However, it is essential for us that those two successive variations Mm' and m'Dshould have *the same sign*, which we write as:

(II)
$$(T = \text{const.}, dp_2 = 0)$$
 $dv_1 \Delta v_2 < 0$

Later on (§ 4.*a*), we shall translate those formulas into ordinary language.

3. – We shall recover those two inequalities in the opposite order in another example. Let a *saline solution* be in the presence of its solvent *vapor*. Recall that at constant temperature the vapor pressure is a *decreasing* function of concentration. Let M (Fig. 2) be the symbolic point for a stable state of the solution-vapor system. As before, we can imagine a transformation that starts from that point M and does not produce any internal modifications. We again separate the two liquids by a diaphragm that transmits the pressure and increase the pressure. The volume will decrease for each of the two fluids, and the symbolic point will displace to m. That will be the first step.

⁽¹⁾ That tendency does not effectively exist in systems that are univariant.

^{(&}lt;sup>2</sup>) That amounts to saying that those modifications are the only ones possible, although they are not necessarily produced.

^{(&}lt;sup>3</sup>) The word "only," whose sense is not always clear, means except for the action of the external cause; here, one has constant volume.



Figure 2.

We then leave the internal transformation that was accomplished by reestablishing contact between the two fluids and waiting for stable equilibrium to be attained.

b') Now keep the pressure constant during the second step. How does one vary the volume?

Since the pressure in the final state A is greater than it is in M, stable equilibrium can be established only under the condition that the solution is more dilute at A that it is at M and m. Compare the two states m and A. The temperature and pressure are the same, so the vapor is in the same state. From m to A, there is dilution, i.e., condensation of a certain quantity of vapor. That internal modification can have only the effect of reducing the volume, which was reduced before between M and m during the first step. Thus, as before:

(II.cont.)
$$(T = \text{const.}, dp_2 = 0)$$
 $dv_1 dv_2 > 0$.

The two illustrated curves for the transformations with or without internal modification have just the relative position that we have represented.

a') As a result, if we imagine the two steps Mm', m'D, the second of which is at constant *volume*, then we will have:

(I)
$$(T = \text{const.}, dv_2 = 0)$$
 $dp_1 dp_2 > 0$,

as above.

4. – As one sees, the question of an isothermal displacement of equilibrium is simply that of *comparing the isotherms* with or without internal modification. That comparison is limited to the neighborhood of a common point M. In reality, one is then comparing the inclinations of the two

curves with respect to the axes or the values of their compressibilities. We shall test that in the examples that are treated and confirm that in a general fashion:

When one starts from a stable state, *the isothermal compressibility is greater when an internal modification has taken place* than when it has not.

That is the statement that contains the essential facts and whose precise mathematical formula we would like to arrive at $(^1)$. I hope that it might be useful to professors and provide a solid basis for them with no need to refer to a proof.

One observes that one can say: When one starts from a stable state, the isotherm without the internal modification will be *more inclined with respect to the v-axis* than the isotherm of the stable state. At least as a mnemonic, one can point out that this is obvious along the isotherm in Fig. 1 since the stable isotherm *BC* is parallel to the *v*-axis.

4.*a*. – Let us translate the inequality (II) into common language.

Instead of translating it directly, it would seem preferable to speak of the *total* variation in volume under the transformation that takes one stable state to another. That variation has the same sign as dv_1 and dv_2 , and it is the sum of them. As a result:

Under a stable isothermal transformation, the variation in volume that is due to only the internal modification has the same sign as the total variation.

That statement seems to me to agree with the elementary facts, and it seems to me that it would be easy for a student that has heard it for the first time to accept it as obvious.

5. Constant pressure. – At this point, one can treat the second law of displacement of equilibrium very briefly.

We are obviously prepared to assume the inequalities that are analogous to the ones that we know already $(^2)$:

(p = const.,	$dQ_2 = 0)$	$dT_1 dT_2 < 0 ,$
(p = const.,	$dT_2 = 0)$	$dQ_1 dQ_2 < 0$

Let us make that precise in an example: For a saturated solution that contains an excess of salt, one separates the solid and the liquid and varies the temperature, and then reestablishes contact between them. In the second step, the solution is put into equilibrium with the salt. That second step can be adiabatic (I) as in an ordinary calorimeter or isothermal (II) if one employs a water bath or an ice calorimeter.

 $(dp_1 + dp_2) dv_2 - dv_1 dp_2 + (dT_1 + dT_2) dS_2 - dS_1 dT_2 \le 0.$

⁽¹⁾ The thermodynamic reason is obvious, moreover. The cycle Mm'D can be described only in the sense that is indicated by the arrows, since m'D is irreversible. It must then be balanced by an absorption of work since it is isothermal. That implies the relative position of MD and Mm.

^{(&}lt;sup>2</sup>) All of the thermodynamic inequalities that we have written down are special cases of the general relation that I have proved:

^{(&}quot;Stabilité et déplacement de l'équilibre," C. R. Acad. Sci. Paris 22 March 1909, pp. 769.)

The general statement is this: *The caloric capacity at constant pressure is greater when an internal modification takes places* then it is when it has not $(^1)$.

One might remember that law by recalling that under a transformation such as evaporation at constant pressure, the caloric capacity is infinite, since the transformation absorbs heat without any variation in temperature.

5.a. – One can further say:

Under a stable transformation at constant pressure, the quantity of heat that is brought into play by the internal modification alone has the same sign that it has for the total transformation $(^{2})$.

6. – The inequalities (II) and the corresponding statements take the form that we spoke of at the beginning, but they are quite different in their appearance from Le Chatelier's principle. That is not entirely new, but it is very less known, such that there is good reason to recall the Le Chatelier himself, in a paper in collaboration with Mouret (Revue Générale des Sciences, 1891), made a statement that was almost identical to the preceding one (³). One sees, moreover, that all that is necessary is a change in the variables that one chooses to express the laws of displacement of equilibrium. One can make even more choices, for example, the one that Le Chatelier stopped with in his recent *Leçons sur le Carbone, la Combustion, le Lois chimiques* that he taught while a member of the science faculty (⁴). The one that I have preferred here in **4.a** and **5.a** seems to me to present the advantage that it involves only two quantities of the same nature in each step, namely, two variations of volume or two quantities of heat.

That change of variable is so simple, but is also has the effect of giving a very new aspect to the laws of displacement of equilibrium, since one sees that what one has too often considered to be absolutely essential in it, like a general law of contrariness, will disappear. It is certain people who know only the first form that Le Chatelier gave to the laws of displacement of equilibrium will tend to believe that any spontaneous transformation will oppose the continuation of the action that provoked it, and that might go so far as to attribute a systematic ill will to nature in that regard. It is time to rehabilitate nature. If it is contrary in certain tendencies then it favors the opposite

$$(p = \text{const.}, \quad dT_2 = 0) \quad dT_1 \, dQ_2 < 0 \,,$$

with our notations. dQ_2 is the heat lost at constant temperature under internal modification. That inequality is distinguished from the ones in the text by the presence of two quantities with a different nature, namely, dT and dQ.

^{(&}lt;sup>1</sup>) Van't Hoff's theorem: Any stable equilibrium displaces under a lowering of temperature towards the system whose formation gives off heat, which will translate into:

^{(&}lt;sup>2</sup>) One must be careful when one applies the laws of displacement of equilibrium outside the cases that we have just examined, and in particular, to transformations at constant *volume*. Indeed, one knows that in a Natterer tube, the same temperature variation can produce condensation or evaporation depending upon the circumstances.

^{(&}lt;sup>3</sup>) Gouy also treated the question with elegance, as well as rigor, in a paper on *useful energy* [J. de Phys. (1888)].

^{(&}lt;sup>4</sup>) One sees how it would be unjust to reproach Le Chatelier for having stopped at just the original form of his statement and make him responsible for the abuse of it that we have made.

tendencies. It is certain that those who would have the objective of realizing a very high pressure by exerting work on a gas must avoid using a gas that is easy to liquify, but we are quite happy that there are liquefiable gases, if only to be able to enclose them in a small volume with less risk of explosion. Similarly, if one proposes to attain a high temperature then one must not use systems whose internal modification will increase the caloric capacity uselessly. However, if we would like to store heat then we can use the phenomena of supersaturation and the release of heat that can be produced at will, as we have begun to do in regard to the heating of trains.

It is likewise an exaggeration to say that everything in nature is good or everything is bad, since it would suffice to recall that any coin has two sides.
