"Über das sogenannte Le Chatelier-Braun Prinzip," Ann. Phys. (Leipzig) (4) 32 (1910), 1102-1106.

## On the so-called Le Chatelier-Braun principle

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In 1884, **Le Chatelier** (<sup>1</sup>) axiomatically expressed a general theorem that related to the changes of state in systems, but it was not correct at the level of generality that **Le Chatelier** had assumed. Independently of **Le Chatelier**, I myself was led to a similar theorem, but I sought to limit its validity more sharply and prove it (<sup>2</sup>). That proof was flawed. I believe that the true content and limits of the theorem shall be established in what follows. In that way, some basically unjustified extensions of it shall be corrected.

A system consists of two components (phases, e.g., salt and a saturated solution of it) that are in equilibrium. Let it be determined by two parameters *x* and *y*. In each component of the system, one parameter *x* is varied by the same amount *dx* and the two system components, thus altered, are brought together again. *Let the equilibrium be displaced by the changes* (cases of indifferent equilibrium are excluded, as before). After recombination, equilibrium is once more established. The system *shall not be able to exchange energy with the environment* during that process. At the time, I had not introduced that auxiliary condition. However, it is essential for the following derivation.

The situation itself is very simple. However, since there is no loss of generality if I base it upon a special example, while the assumptions will be expressed more clearly by that, let the chosen system be salt and a saturated solution of it. Let the parameters be pressure p and t.

A. – For the sake of simplicity, set p = 0. The salt and the solution might be heated by  $\Delta t$  separately from each other. Let *E* be the total internal energy of the two system components. An internal energy of:

(a)

$$\frac{dE}{dt}\Delta t$$

has been added to the system.

Both parts are now brought back together again, while being prevented from exchanging any energy with each other.

<sup>(&</sup>lt;sup>1</sup>) Le Chatelier, C. R. Acad. Sci. Paris **99** (1884), 788.

<sup>(&</sup>lt;sup>2</sup>) **F. Braun**, Göttinger Nachrichten, 7 Sept. 1887; Ann. Phys. (Leipzig) **33** (1888), pp. 337.

Now, if the system is once more put into equilibrium then it will adjust to a different temperature  $t + \overline{\Delta t}$ , and an amount of salt  $dm_1$  will precipitate or dissolve. By assumption, one will then have:

(b) 
$$\frac{\partial E}{\partial t}\overline{\Delta t} + \frac{\partial E}{\partial m_1}dm_1 = \frac{\partial E}{\partial t}\Delta t.$$

In the event that  $(\partial E / \partial m_1) dm_1$  is positive, it will follow immediately that  $\overline{\Delta t} < \Delta t$ , i.e., the parameter that was changed arbitrarily by  $\Delta t$  will perform a retrograde motion during the transition to the new equilibrium position, as was postulated in the principle that we speak of. The condition that the system must be continuously variable, which was the foundation for that analysis, is satisfied.

However, the same condition can also be satisfied (purely energetically) when the arbitrary change  $\Delta t$  takes place along a certain line segment in the same (positive) sense) and then stops. It will follow from (b) that:

$$\frac{\partial E}{\partial t}(\overline{\Delta t} - \Delta t) = -\frac{\partial E}{\partial m_1} dm$$

 $\partial E / \partial t$  is positive, while  $\overline{\Delta t} - \Delta t$  can also be positive when the right-hand side is positive, and nothing can be said about the latter *a priori*.

Let us introduce an auxiliary concept here (that can perhaps be regarded as an axiom). The physical process is obviously the following: Due to the fact that both phases have been heated by  $\Delta t$  (and then brought together again), the equilibrium will be displaced, and establishing the new equilibrium will imply a change in temperature. However, that cannot again be a rise in temperature for a continuously-varying system, because if the transition into a new equilibrium position is first required by an externally-produced rise in temperature then it would seem unnatural that the cause of the process would again be raised by its effect. The system would not be a continuously-varying one (at least, within a certain region). The change ( $\partial E / \partial m_1$ )  $dm_1$  in internal energy would be finite.

B. – One has the same system and changes the pressure p in the two phases by  $+\Delta p$  at constant temperature. One then brings the phases together again under the given conditions (so adiabatically and at constant volume). One will now have:

(c) 
$$\frac{\partial E}{\partial p} \Delta p = \frac{\partial E}{\partial p} \overline{\Delta p} + \frac{\partial E}{\partial m_1} dm_1 + \frac{\partial E}{\partial t} dt,$$

with analogous notations.

The same consequences are true here. The total amount:

$$\frac{\partial E}{\partial m_1} dm_1 + \frac{\partial E}{\partial t} dt$$

must be positive, since otherwise  $\Delta p$  would increase, etc.

The theorem is applicable to all systems that are so arranged that one can (mentally) separate the components and change just one parameter in each of them. The parameter that is changed arbitrarily, but infinitely-little, must then change in the opposite way while equilibrium is being established. All that means is that the internal energy that is added to the system, and which brings about the change in equilibrium, will be partially converted into a second type of energy. The new equilibrium state is made possible only by increasing the second type through a well-defined, but likewise infinitely-small, amount, and conversely the continuous variability of the system is also made possible only by those conditions.

Systems of that type also include, e.g., a galvanic element and a condenser that is charged by it.

For many systems, such as salt and salt solution, the parameters of the fixed phase (viz., pressure and temperature) can change in the positive and negative senses, while those of liquids can change with that degree of generality only because we also know of solutions in a state of supersaturation. In other systems, such as ice and water, solid and molten paraffin, the variation of the parameter in the solid phase is even more restricted (<sup>1</sup>). Nonetheless, the theorem is still applicable. One can, e.g., imagine that the temperature has been brough below the freezing point in both phases. Experiments (with supercooled water) then show that each phase will continue to exist by itself with no change of phase. Likewise, one can always find a (positive or negative) change in pressure that satisfies that condition.

By contrast, for one-phase systems, we do not know whether it is possible to change one parameter (e.g., pressure) arbitrarily and first affect the other one (say, temperature) in that way. One would be able to extend the theorem to those systems only by means of a fiction whose justification has not been proved. On the other hand, and on the same grounds, the facts do not contradict the principle (even where it might seem as if, e.g., a rise in pressure is coupled with an increase in temperature that acts like a higher pressure, in its own right). Compared with systems to which we can apply it (since we can separate the processes in time and also always, in fact, find that it is verified for them), when it is not possible to make that separation, we will, in fact, be in the same position that we were in with one-phase systems. A more general theorem might exist then, but we are in a position to establish it experimentally only for certain types of systems.

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<sup>(&</sup>lt;sup>1</sup>) In general, one can also realize superheated ice when one raises the pressure, and it would be interesting to pursue the temporal amount of change in the internal energy that is produced by raising the pressure in terms of molecules. Superheated ice is also present in the known experiment where a thin loaded wire cuts through a block of ice. The total change in internal energy is equal to zero in that case.