“Das Prinzip von Le Chatelier-Braun und die Reciprocitätssätze der Thermodynamik,” Zeit. phys. Chem. **77** (1911), 227-244.

The Le Chatelier-Braun principle and the reciprocity laws of thermodynamics

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Contents

The following arguments (1) arose from the desire to find a criterion for how one must apply the **Le Chatelier-Braun** principle in each special case in order to arrive at the expected effect with the *correct* sign, and not the *opposite* one (2). The results that were thus obtained are summarized at the conclusion of the present article.

§ 1. The usual formulation of the principle (3). –Ordinarily, one puts forth the formulation of the principle as something that is illustrated by perhaps the following example: A given quantity of an ideal gas is compressed:

I. *Isothermally* (i.e., at constant T) while one raises the external pressure by δp ; that will produce a change in volume of $\delta_{\mathrm{I}} v$.

II. *Adiabatically* (i.e., "T will be left alone") while one raises the external pressure by δp ; that will produce a change in volume of $\delta_{\mathrm{II}} v$.

The absolute values of the changes $| \delta_{\mathrm{I}} v |$ and $| \delta_{\mathrm{II}} v |$ satisfy the following inequality:

$$| \delta_{\mathrm{II}} v | < | \delta_{\mathrm{I}} v | . \tag{1}$$

Therefore, the *directly-affected* parameter exhibits a greater *capacity to resist* the increase in pressure in the second case than it does in the first one. In the second case, the other state parameter (T) is, in a sense, an "auxiliary" to the directly-affected one (v).

Le Chatelier and **Braun** have proposed the following general principle as an abstraction of a series of concrete examples that all have the same type as the example that was just cited: Let the *stable* equilibrium of a thermal system be determined by arbitrary parameters a, b, c, … One further assumes that none of the parameters can change, except for two of them (say, ρ and σ). An external cause (the pressure increase δp, in the example) influences the parameter ρ *directly* (v, in the example). The other parameter σ (T, in the example) will be fixed in one case (Experiment I), while it is free in the other, i.e., "it is left alone" (Experiment II).

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(1) The present treatise appeared in Russian in Autumn 1909: Jour. d. russ. physic. Ges. **41** (1909), 347. At the time of its writing (Summer 1909), I was unaware of the paper by **C. Raveau** ["Les lois du déplacement de l'équilibre et le principe de Le Chatelier," Jour. d. phys. **8** (1909), 572] that had appeared shortly before. That paper has some points in common with § **4** of the present paper, but only there. Some other papers have appeared on the Le Chatelier-Braun principle in recent times, namely: **F. Braun**, "Über das sogennante Le Chatelier-Braun Prinzip," Ann. Phy. (Leipzig) (4) **32** (1910), 1102; **A. Leduc**, "Application du principe de Lenz aux phénomènes qui accompagnent la charge des condensateurs," C. R. Acad. Sci. Paris **152** (1911), 313. None of those papers led to a resolution of the question.

(2) I was led to address that question when **V. R. Bursian** (a student at the University of St. Petersburg, at the time) drew my attention to the fact that the examples that one ordinarily cites as evidence for the **Le Chatelier-Braun** principle exhibit contradictory behavior.

(3) **Le Chatelier**, C. R. Acad. Sci. Paris **99** (1884), 786; *ibid.*, **104** (1887), 679; **F. Braun**, Zeit. f. phys. Chem. **1** (1887), 259); Wied. Ann. **33** (1888), 337; **W. Nernst**, Theoret. Chemie (1898), 611; **O. D. Chwolson**, *Lehrbuch der Physik* **3**, Chap. VIII, § **11**, 1905; **B. Weinstein**, Thermodyn. **1** (1901), 29, "Prinzip der möglichsten Erhaltung des Zustands."

The principle is then stated:

In the second case, the conjugate parameter σ changes in such a way that the (absolute value of the) change in the directly-affected parameter ρ will prove to be smaller than it is in the case where σ is kept fixed.

$$| \delta_{\mathrm{II}}\rho | < | \delta_{\mathrm{I}}\rho | . \tag{2}$$

($\delta_{\mathrm{I}}\rho$ is at constant σ, while σ is "left alone" for $\delta_{\mathrm{II}}\rho$) The "resistance of the system to external influences" then increases due to the assistance of the parameter σ.

Naturally, one recognizes a clear analogy with **Lenz**'s law of electrodynamics in that principle ([1]).

§ 2. Proof of the invalidity of the usual formulation on the basis of examples. – On grounds that will be first explained completely later on, it is very easy to give examples in which phenomena proceed *in strict contradiction to the **Le Chatelier-Braun** principle*. We choose the simplest example: Suppose that an elastic rectangular parallelepiped is given: Its state at any time-point is determined by the following parameters: Temperature T, height x_1, width x_2, thickness x_3. Let x_3 and T be totally invariable. A force δk strives to increase x_1. (x_1 is then the directly-affected parameter ρ of the system.)

Experiment I: The parameter x_2 (viz., the width) is kept constant. Let $\delta_{\mathrm{I}} x_1$ be the increase in height that results from δk .

Experiment II: The parameter x_2 is "left alone." In that case, δk will produce the elongation $\delta_{\mathrm{II}} x_1$.

The **Le Chatelier-Braun** principle states that:

$$| \delta_{\mathrm{II}}\, x_1 | < | \delta_{\mathrm{I}}\, x_1 | . \tag{3}$$

In fact, one has precisely the converse:

$$| \delta_{\mathrm{II}}\, x_1 | > | \delta_{\mathrm{I}}\, x_1 | . \tag{4}$$

([1]) While formulating his own principle**, Le Chatelier** mentioned that **G. Lippmann** had developed an analogous idea in the special case of electrical phenomena. **G. Lippmann** ["Principe de la conservation de l'électricité," Ann. Chim. Phys. **24** (1881)], in his own right, referred to **Lenz** in Akad. d. Wiss. zu Petersburg 29.XI.1833, printed in Pogg. Ann. **31** (1834), 483. Cf., the almost simultaneous paper of **Ritchie**, *ibidem*, pp. 203. The latter got precisely the wrong the sign for all cases of induction. **Lenz** derived his principle in a purely-inductive way, while **Ritchie** deduced his statements from a type of generalized "principle of the equality of action and reaction." (**Ritchie** did not notice his mistake. It was first pointed out by **Poggendorf** when he published the papers of **Lenz** and **Ritchie** in succession.)

This much is known from the elements of the theory of elasticity ([1]): When the lateral dimension x_2 is "left alone," a certain traction will produce a greater elongation of the prism than for fixed x_2 . Thus, when we apply the terminology that was employed above to the present case, we must say: The *conjugate* parameter x_2 will *decrease*, which will change the "capacity to resist" of the *directly-affected* parameter x_1, which is in direct contradiction to the statement of the **Le Chatelier-Braun** principle.

Moreover, the majority of examples that **Le Chatelier** and **Braun** cited as evidence of their principle exhibited basically the same property: In the form that the individual examples were presented *directly*, the principle directly exhibited a contrary behavior, and the examples could be made to agree with the principle only by means of a suitable formulation. The reason why virtually the majority of examples exhibited that behavior will become understandable later on (end of § **5**)([2]).

§ 3. The proof of the principle that Braun gave. – **Le Chatelier**, as well as **Braun** (in his first papers), formulated the principle and applied it with *very great* success in their experimental investigations without seeking to derive that the principle from deeper fundamental laws. It was only later that **Braun** ([3]) verified that *his principle is an immediate consequence* of the assumption that the *equilibrium state in question is stable*.

One might expect from the outset that a careful analysis of the method of proof must shed some light on the question of how the examples that were cited in § **2** can be made to agree with the principle. In order to simplify the argument, **Braun** mainly introduced the following *fiction:* In Experiment II, the new equilibrium state should not be established immediately after the effect of the external cause, but by a series of temporally-discrete intermediate states that are also in very rapid succession. The directly-affected parameter ρ initially changes by itself, i.e., at constant parameter σ. The yields a first change of $\rho : \delta_1\rho$. What then results is a corresponding first change in the parameter $\sigma : \delta_1\sigma$. That change produces a second change in $\rho : \delta_2\rho$, which brings a second change in $\sigma : \delta_2\sigma$, along with it, etc.

([1]) See, e.g., **Chwolson**, *Lehrbuch de Physik* **1**, Sec. **6**.

([2]) Here, we would like to mention two more examples of other types of applications:

a) *The dissociation of iodine vapor.* – The temperature is kept constant unconditionally. External influence: raising the external pressure by δp . Directly-affected parameter (ρ): the volume v. Conjugate parameter (σ): degree of dissociation α . Here, the **Le Chatelier-Braun** principle then asserts: α changes in such a way that $|\delta v|$ will prove to be smaller than the $|\delta v|$ that would occur in the event that one could keep the degree of dissociation α unchanged (by some sort of *fictitious* mechanism). That is because, from the principle, the induced change in the conjugate parameter a should indeed *raise* the "capacity to resist" of the directly-affected parameter v. The principle the demands that iodine vapor should react to an *increase* in the external pressure with an *increase* in the dissociation (when T is kept constant!). Naturally, a decrease in the dissociation occurs in reality (**van't Hoff**, 1885).

b) *The behavior of a two-phase system.* – Mass-unit of water: x in its fluid phase, $1 - x$ in the vapor phase. T is kept unconditionally constant. External influence: Raising the external pressure by $\delta p : \rho = v,\ \sigma = x$. The principle demands that: x changes in such a way that $|\delta v|$ proves to be smaller than the $|\delta v|$ that would occur in the event that one could keep x unchanged (by a *fictitious* mechanism), because… The principle then demands that the system must react to a *raising* of the external pressure (when the temperature T is kept constant!) with a further *evaporation* of the fluid. Naturally, the opposite thing happens in reality: viz., condensation. For further examples, see **Chwolson**, *Lerhbuch der Physik*, **3**, 476-480.

([3]) Wied. Ann. **33** (1888), 337.

The gist of the entire proof is then the statement that $\delta_2\rho$ *always has the opposite sign to* $\delta_1\rho$. That is coupled with the following argument: If $\delta_2\rho$ had the same sign as $\delta_1\rho$ then the original change would increase to the higher value $\delta_1\rho + \delta_2\rho$. Furthermore, $\delta_1\rho$ would then cause the change $\delta_3\rho$ to again have the same sign as $\delta_1\rho$ and $\delta_2\rho$. *In that way, the changes in the variables would grow to finite values by themselves*, but that would contradict the assumption of a stable equilibrium.

When we test that argument in the example of the elastic prism, we see immediately that the successive changes in the directly-affected parameter x_1 all have the same sign, without sacrificing stability ([1]). *The proof of the principle that* ***Braun*** *gave is therefore inconclusive.*

§ 4. The necessity of a precise restriction on the choice of parameter. – When one next seeks a new consistent formulation of the principle by a purely-inductive method, one will soon feel the lack of a precise statement of it that would infer ρ and σ as state parameters from the physical quantities when the principle is applied. In order to explain that remark, we appeal to the example that we started with in § **1**.

Thermal system: an ideal gas. Conjugate phenomena: Expansion by heat, cooling by contraction. Initially, four physical state quantities will serve as possible parameters ρ and σ: volume v, temperature T, pressure p, entropy S. It is not necessary for our purposes to consider other parameters. Eight combinations (ρ, σ) are summarized in the following table:

Table 1.

(ρ, σ)	(v, T)	(v, S)	(p, T)	(p, S)	(T, v)	(T, p)	(S, v)	(S, p)
Given change	δp	δp	δv	δv	δS	δS	δT	δT
Experiment I	$\delta T = 0$	$\delta S = 0$	$\delta T = 0$	$\delta S = 0$	$\delta v = 0$	$\delta p = 0$	$\delta v = 0$	$\delta p = 0$
Experiment II	$\delta S = 0$	$\delta T = 0$	$\delta S = 0$	$\delta T = 0$	$\delta p = 0$	$\delta v = 0$	$\delta p = 0$	$\delta v = 0$
Resulting inequality	$\lvert \delta_{\mathrm{II}} v \rvert < \lvert \delta_{\mathrm{I}} v \rvert$	$\lvert \delta_{\mathrm{II}} v \rvert > \lvert \delta_{\mathrm{I}} v \rvert$	$\lvert \delta_{\mathrm{II}} p \rvert > \lvert \delta_{\mathrm{I}} p \rvert$	$\lvert \delta_{\mathrm{II}} p \rvert < \lvert \delta_{\mathrm{I}} p \rvert$	$\lvert \delta_{\mathrm{II}} T \rvert < \lvert \delta_{\mathrm{I}} T \rvert$	$\lvert \delta_{\mathrm{II}} T \rvert > \lvert \delta_{\mathrm{I}} T \rvert$	$\lvert \delta_{\mathrm{II}} S \rvert > \lvert \delta_{\mathrm{I}} S \rvert$	$\lvert \delta_{\mathrm{II}} T \rvert > \lvert \delta_{\mathrm{I}} T \rvert$

Remarks:

1. One convinces oneself of the validity of the resulting inequalities immediately on the basis of the known properties of ideal gases.

([1]) Here, one can proceed as follows: First, an elongation δx at fixed x_2 ; x_1 might then experience an increment $\delta_1 x_1 = + \varepsilon$. We then fix x_1 and leave x_2 to itself. x_2 will be reduced a little by that: $\delta_1 x_2 = - q\,\varepsilon$. If we now again fix x_2 and leave x_1 to itself then x_1 will *lengthen* by $\delta_2 x_1 = + q^2\,\varepsilon$, etc. All of the successive changes $\delta_h x_1$ will have *the same* sign. However, they will define a convergent geometric progression, and as a result one will *not get any sort of growth to a finite value.*

2. "Given change." As soon as one establishes which of the quantities should serve as the directly-affected parameter ρ, it is also clear what sort of "influence" one is speaking of. For example, if ρ is p then the immediate influence on p consists of prescribing the change δv in the volume. When $\rho = T$, the immediate influence on T consists of the addition of a quantity of heat δQ, or what amounts to the same thing for all reversible changes (and we shall consider only such things here), the addition of a quantity of entropy δS, etc.

3. "σ kept constant," "σ left alone." The first expression clearly means: $\delta\sigma = 0$. Once we have first agreed upon which state quantity should be the one "with a variable parameter σ," it will obviously be also established what we would like to regard as Experiment I. – By its very nature, the expression "σ is left alone" is much less well-defined. In some cases, one can generally use it in the sense that is ordinarily implied, e.g., T is left alone means an adiabatic change: $\delta S = 0$. v is left alone means isopiestic change $\delta p = 0$. In other cases (e.g., $\sigma = S$, $\sigma = p$), all that remains is to proceed by analogy with the foregoing cases: S is left alone means $\delta T = 0$. p is left alone means $\delta v = 0$. In any case, the arbitrariness in those interpretations shows how ill-defined that expression is, which plays such an essential role in the formulation of the **Le Chatelier-Braun** principle.

4. If we understand ρ to mean the same parameter twice, but while choosing the co-varying parameter σ to be T in one case and S in the other or v in one case and p in the other then that would imply a *permutation* of the physical senses of Experiments I and II. Naturally (as Table I shows), that inversion corresponds to an inversion of the inequality signs for the transitions $(v, T) \to (v, S)$, $(p, T) \to (p, S)$, $(T, v) \to (T, p)$, $(S, v) \to (S, p)$.

5. If we choose σ to mean the same parameter twice but let ρ go from $\rho = v$ to $\rho = p$ or from $\rho = T$ to $\rho = S$, respectively, then we will confirm the *formal* inversion of the inequality sign in each case. However, as far as the *physical* sense of the inequalities that are obtained is concerned, we must consider the following:

a) The inequalities:

$$| \delta_{\mathrm{II}}\, v | < | \delta_{\mathrm{I}}\, v | \qquad \text{and} \qquad | \delta_{\mathrm{II}}\, p | < | \delta_{\mathrm{I}}\, p | \tag{5}$$

mean the same thing *physically* as saying that the "elastic capacity" in Experiment II (if we may speak of such a thing) is *smaller* than it is in Experiment I.

b) The inequalities:

$$| \delta_{\mathrm{II}}\, T | < | \delta_{\mathrm{I}}\, T | \qquad \text{and} \qquad | \delta_{\mathrm{II}}\, S | < | \delta_{\mathrm{I}}\, S | \tag{5}$$

mean one and the same thing *physically*, namely, that the *thermal capacity* is *greater* in Experiment II than it is in Experiment I.

6. "Increase in the resistance." The first of inequalities (5) exhibits the same inequality sign as the inequality (*a*) in § **1**, but the second one exhibits the opposite one. If one disregards that then one will be forced to interpret both inequalities in the same way, namely: The system in Experiment II exhibits a *greater* resistance than the one on Experiment I. Otherwise, the word "resistance" would forfeit any physical sense whatsoever. However, it would then be clear that the inequality:

$$|\delta_{\mathrm{II}}\,\rho| < |\delta_{\mathrm{I}}\,\rho|\,,$$

which should, in fact, be *always* true, from the **Le Chatelier-Braun** principle, would demand the opposite behavior for the system according to whether one had chosen $\rho = v$ or $\rho = p$. Ultimately, as far as the inequalities (6) are concerned, it is already entirely arbitrary here what one would like to regard as an increased or diminished capacity to resist.

To recapitulate, one then sees that: When one goes from one choice of parameter (ρ, σ) to another, one can invert:

1. The physical sense of what one would like to call Experiment I and Experiment II.

2. The physical interpretation of the resulting inequality sign in the sense of increasing or decreasing "capacity to resist" in Experiment II. Thus, if a generally-valid formulation of the **Le Chatelier-Braun** principle is to be possible at all then it would not be possible without a precise choice of the system of parameters. *Since **Braun** did not impose such a restriction on the choice of parameters in his proof, that would exclude the possibility that his proof could lead to that objective.*

§ 5. The usual choice of parameter and its relationship to the Le Chatelier-Braun principle. – For the sake of convenience of measurement, the following quantities will first serve as the state parameters for the elastic prism that was considered in § **2**: T, x_1, x_2, x_3 . From an energetic standpoint, the quantities x_1, x_2, x_3 possess the following peculiarity: *If all of the quantities x remain constant (for an arbitrarily-varying T) then no exchange of work between the given system and external world will result.*

Let y_1, y_2, y_3 be the forces that seek to increase the dimensions x_1, x_2, x_3 of the elastic prism (for a certain state of compression). The system of parameters T, y_1, y_2, y_3 would already no longer obey the energy constraint: When T varies at constant y_1, y_2, y_3, the dimensions x_1, x_2, x_3 will vary as a result, and the principle will then imply that work is done. One can also define the quantities y_1, y_2, y_3 to be the coefficients of δx_1, δx_2, δx_3 in the expression for the infinitely-small amount of work that is done by the system:

$$\delta A = y_1\,\delta x_1 + y_2\,\delta x_2 + y_3\,\delta x_3\,.$$

According to experiments (!), in order to characterize the equilibrium state of any thermal system, one can choose the T, along with those state parameters x_1, …, x_n that possess the aforementioned energetic property ([1]). *in what follows, we will apply the notation* $x_1, x_2, \ldots, x_n$ *to those parameters with that character exclusively.* The infinitely-small amount of work that the system performs when one goes from the state $T, x_1, \ldots, x_n$ to the state $T + dT, x_1 + dx_1, \ldots, x_n + dx_n$ will then be expressed by the formula:

$$dA = \sum y_h \, dx_h \,,$$

which includes no term of the form $\Theta \, dT$. The quantities $y_1, \ldots, y_n$ are the generalization of the forces y_1, y_2, y_3 in the case of the elastic prism (and the pressure in the case of gases). One can probably say that, *in general*, thermodynamic investigations will employ precisely the system of parameters $T, x_1, \ldots, x_n$ most often, but in each case they will serve as the initial system.

The resulting inequalities are summarized in the following table for the three typical combinations (ρ, σ) that are possible for the aforementioned choice of parameters.

Table 2.

(ρ, σ)	(x_h, T)	(T, x_k)	(x_h, x_k)
Given change	δy_h	δS	δy_h
Experiment I	$\delta T = 0$	$\delta x_k = 0$	$\delta x_k = 0$
Experiment II	$\delta S = 0$	$\delta y_k = 0$	$\delta y_k = 0$
Resulting inequality	$\lvert \delta_{\mathrm{II}} x_h \rvert \leq \lvert \delta_{\mathrm{I}} x_h \rvert$	$\lvert \delta_{\mathrm{II}} T \rvert \leq \lvert \delta_{\mathrm{I}} T \rvert$	$\lvert \delta_{\mathrm{II}} x_h \rvert \leq \lvert \delta_{\mathrm{I}} x_h \rvert$

Remarks:

1. Later on, we will show that the cited inequalities can prove to be entirely general. For the moment, it will suffice to test them in the individual examples, e.g., in the case of an elastic prism.

2. The third inequality has the opposite sign to the inequality (α) in § **1** ([†]). When we let h and k run through all values from 1 to n, we will get n $(n - 1)$ different cases of that inequality.

3. The first and second inequalities agree with the inequality (α) in § **1**, as far as their senses of direction are concerned. They represent $2n$ cases.

4. As far as the interpretation of the various inequalities in the sense of "increased resistance" is concerned, one can confer Remark 6 concerning Table 1.

([1]) **Helmholtz**: "Die Thermodynamische-chemische Vorgänge," (1882) (**Ostwalds** Klassiker, no. 124, or *Ges. Abh.* III, pp. 958.) in "Nachträgliche Zusatz." – **H. A. Lorentz** (*Ges. Abh.*) "Über den II. H_d S," § **11**.

([†]) Translator: I did not find the inequality (α) in the original; I suspect it refers to equation (1).

We can then say that *for the most common choice of parameter, namely, the choice* $T, x_1, \ldots, x_n$, *the inequality* (a) *in* § **1** *will be fulfilled in only* $2n$ *cases, whereas the opposite inequality sign will obtain in* $n\,(n-1)$ *cases*. Agreement is always present only for $n = 1$.

§ 6. The parameter system $S, x_1, \ldots, x_n$. – If we recall the remarks concerning Tables 1 and 2 then we will, with no further discussion, be in a position to select system of parameters such that all of the resulting inequalities already exhibit one and the same sense of direction. We would first like to consider the parameter system $S, x_1, x_2, \ldots, x_n$. The corresponding Table looks like:

Table 3.

(ρ, σ)	(x_h, S)	(S, x_k)	(x_h, x_k)
Given change	δy_h	δT	δy_h
Experiment I	$\delta S = 0$	$\delta x_k = 0$	$\delta x_k = 0$
Experiment II	$\delta T = 0$	$\delta y_k = 0$	$\delta y_k = 0$
Resulting inequality	$\lvert \delta_{\mathrm{II}}\, x_h \rvert \leq \lvert \delta_{\mathrm{I}}\, x_h \rvert$	$\lvert \delta_{\mathrm{II}}\, S \rvert \leq \lvert \delta_{\mathrm{I}}\, S \rvert$	$\lvert \delta_{\mathrm{II}}\, x_h \rvert \leq \lvert \delta_{\mathrm{I}}\, x_h \rvert$

Remarks:

1. Those three types of inequalities collectively represent $2n + n\,(n-1)$ cases. *They all have the opposite sense of direction to the inequality* (α) *in* § **1**.

2. If we recall the example of the elastic prism [$n = 3$, $2n + n\,(n-1) = 12$] then we can formulate the physical sense of the twelve inequalities that are obtained as follows: *For the choice of parameter system* $S, x_1, x_2, \ldots, x_n$, *Experiment II corresponds to a* ***greater*** *thermal (elastic, resp.) capacity than Experiment I in all twelve cases.*

§ 7. The parameter system $T, y_1, y_2, \ldots, y_n$. – One finds the resulting inequalities for that choice of parameters in the following table:

Table 4.

(ρ, σ)	(y_h, T)	(S, y_k)	(y_h, y_k)
Given change	δx_h	δS	δx_h
Experiment I	$\delta T = 0$	$\delta y_k = 0$	$\delta y_k = 0$
Experiment II	$\delta S = 0$	$\delta x_k = 0$	$\delta x_k = 0$
Resulting inequality	$\vert \delta_{\mathrm{II}}\, y_h \vert \geq \vert \delta_{\mathrm{I}}\, y_h \vert$	$\vert \delta_{\mathrm{II}}\, T \vert \geq \vert \delta_{\mathrm{I}}\, T \vert$	$\vert \delta_{\mathrm{II}}\, y_h \vert \geq \vert \delta_{\mathrm{I}}\, y_h \vert$

Remarks:

1. Just as in Table 3, all inequalities have the opposite signs to the inequality (*a*) in § **1**.

2. If we recall the example of the elastic prism then we can formulate the physical content of the resulting twelve inequalities as follows: *For a choice of the parameter system T, y_1, …, y_n , Experiment II will correspond to a* ***smaller*** *thermal (elastic, resp.) capacity then in Experiment I in all twelve cases.*

The apparent contradiction between that result and the result of § **6** will disappear when one observes that Experiment I will go to Experiment II and Experiment II will go to Experiment I under the transition from S, x_1, …, x_n to T, y_1, …, y_n .

§ 8. Introducing the concepts of intensity and quantity parameters. – The results of the last three paragraphs can be easily summarized with the help of the **Mach-Helm-Ostwald** distinction between "intensity" and "quantity" parameters ([1]). I could not find any satisfactory definitions of those concepts in the literature, nor could I come up with ones. For that reason, we must perhaps restrict ourselves to characterizing those concepts by examples in the usual way. Examples of *intensity* parameters are pressure, elastic forces (viz., stress), the capillarity constant, the potential in a conductor, the electromotive force in an element, and osmotic pressure. Examples of *quantity* parameters are volume, deformation (strain), surface area, quantity of electricity, the time integral of current, concentration.

To the extent that the concepts of intensity and quantity parameters are defined by those examples at all, one can also classify the parameters x_1, …, x_n and y_1, …, y_n that were mentioned in **5**, the former as quantity parameters and the latter as intensity parameters. In addition, T naturally belongs to the intensities, while S belongs to the quantities. In that way, the three parameter systems that were considered up to now can be characterized as follows:

$$S, x_1, \ldots, x_n \qquad \text{system of pure quantities,}$$

([1]) **G. Helm**, *Energetik*, Leipzig, 1898, pp. 266.

$T, y_1, \ldots, y_n$ system of pure intensities,
$T, x_1, \ldots, x_n$ mixed system.

The resulting inequalities always have one and the same sense of direction for the two pure systems. For the mixed parameter system, the combinations (T, x_k) and (x_h, T) will yield *one* sense of direction and the combinations (x_h, x_k) will yield the opposite one.

§ 9. Systematic analysis of the Le Chatelier-Braun principle on the grounds of the thermodynamic reciprocity laws. – Whereas we have proceeded inductively up to now, we would now like to prove the statements that were achieved on the basis of the first two laws of thermodynamics and generalize them. Our path will first lead us to the reciprocity laws of thermodynamics ([1]).

Let:

$$\delta A = \sum_{h=1}^{n} y_h \, \delta x_h \tag{7}$$

be the work that thermal system *performs* under an infinitely-small change of state and let δQ be the amount of heat that it *receives* in so doing. If U is the energy and S is the entropy of the system then:

$$\text{(First fundamental law)} \qquad \delta U = \delta Q - \delta A, \tag{8}$$

$$\text{(Second fundamental law)} \qquad \delta Q = T \, \delta S \, . \tag{9}$$

Hence, from (7), (8), (9):

$$\delta U = T \, \delta S - \sum_{h=1}^{n} y_h \, \delta x_h \, . \tag{10}$$

The aforementioned reciprocity laws will be derived from the requirement that δU must be a complete differential:

$$\frac{\partial T}{\partial x_h} = -\frac{\partial y_h}{\partial S} , \qquad \frac{\partial y_h}{\partial x_k} = \frac{\partial y_k}{\partial x_h} . \tag{11}$$

For the sake of what follows, we likewise add the inequalities:

$$\frac{\partial T}{\partial S} \geq 0, \qquad \frac{\partial y_k}{\partial x_h} \geq 0, \tag{12}$$

([1]) See, e.g., *Enzykl. d. math. Wiss.*, v. 3, **Bryan**, *Thermodynamik*.

which one obtains (1) when one imposes the demand that the equilibrium in question should not be labile (so it will be stable, or at least indifferent). The relations (11), (12) then take on a much clearer appearance when one sets (2):

$$x_0 = -S\,, \tag{13}$$
$$y_0 = +T\,. \tag{14}$$

(10), (11), (12) can then be written as follows:

$$\begin{array}{c} \text{Parameter} \\ x_0, x_1, \ldots, x_n \end{array} \left\{ \begin{array}{ll} \delta U = -\sum_{h=0}^{n} y_h\, \delta x_h\,, & \text{(A)} \\ \dfrac{\partial y_h}{\partial x_k} = \dfrac{\partial y_k}{\partial x_h}\,, & \text{(B)} \\ \dfrac{\partial y_h}{\partial x_h} < 0\,. & \text{(C)} \end{array} \right.$$

It will then be easy to go over to the other parameters. One first takes the parameters to be y_0 (= T), $y_1, \ldots, y_n$ (3):

$$\begin{array}{c} \text{Parameter} \\ y_0, y_1, \ldots, y_n \end{array} \left\{ \begin{array}{ll} \delta\left(U + \sum_{h=0}^{n} y_h\, x_h\right) = \sum_{h=0}^{n} x_h\, \delta y_h\,, & \text{(A}'\text{)} \\ \dfrac{\partial y_h}{\partial x_k} = \dfrac{\partial y_k}{\partial x_h}\,, & \text{(B}'\text{)} \\ \dfrac{\partial y_h}{\partial x_h} \leq 0\,. & \text{(C}'\text{)} \end{array} \right.$$

Finally, we would also like to consider the most general case of a *mixed* system: The case in which the parameter is taken to be any t of the quantities y and those $(n + 1 - t)$ quantities x for which the remaining y'_s are coefficients in the expression for δA. We would like to denote the former of those quantities by $\eta_1, \eta_2, \ldots, \eta_t$ and the latter by $x_{t+1}, \ldots, x_{n+1}$, in which the indices might have an entirely different meaning from what they had in the previously-considered cases. We then get:

(1) The first inequality says that the temperature does not drop in any case when one adds heat to the body while x'_s is held constant. The second inequality says that the force y that seeks to *increase* x will decrease, or at least remain constant when x increases.

(2) The generally-accepted method for defining *heat lost* and *work done* by the body is inconsistent and is probably explained historically only by the origins of thermodynamics in mechanical engineering. The conventions (13), (14) compensate for that inconsistency and, at the same time, allow it to emerge that entropy is a quantity, while temperature is an intensity.

(3) The transition from (A) to (A′) and then to (A″) is the same as the (*Legendre*) contact transformation by which one goes from the *Lagrangian* to the *Hamiltonian* equations in mechanics.

$$\text{Parameter}\quad \begin{matrix}\eta_1,\ldots,\eta_t\\ x_{t+1},\ldots,x_{n+1}\end{matrix}\quad\left\{\begin{array}{ll} \delta A = \sum \eta_r\,\delta\xi_r + \sum y_h\,\delta x_h & (4'') \\ \delta\left(U + \sum \eta_r\,\xi_r\right) = \sum \xi_r\,\delta\eta_r - \sum y_h\,\delta x_h, & (\mathrm{A}'') \\ \dfrac{\partial\xi_r}{\partial\eta_s} = \dfrac{\partial\xi_s}{\partial\eta_r},\quad \dfrac{\partial\xi_r}{\partial x_h} = -\dfrac{\partial y_h}{\partial\eta_r},\quad \dfrac{\partial y_h}{\partial x_k} = \dfrac{\partial y_k}{\partial x_h}, & (\mathrm{B}'') \\ \dfrac{\partial\xi_r}{\partial\eta_r} \le 0;\quad \dfrac{\partial y_h}{\partial x_h} \le 0, & (\mathrm{C}'') \end{array}\right.$$

Remarks:

1. Depending upon one's choice of parameters, the thermodynamic potential will be replaced with one of the following functions:

$$U, \qquad U + \sum_{h=0}^{n} y_h\,x_h\,, \qquad U + \sum_{r=0}^{t} \eta_r\,\xi_r\,.$$

The reciprocity laws (B), (B′), (B″) are the necessary and sufficient conditions for their existence.

2. It is worth noticing that the right-hand and left-hand sides in the middle of equations (B″) have opposite signs.

§ 10. Continuation. – With the help of the notations (13), (14), the entirely of Table 3 can be reduced to its last column, except that h must run from 0 to n + 1. In that way, *the resulting inequalities in Table 3 will take on a unified appearance, namely:*

$$|\,\delta_{\mathrm{II}}\,x_h\,| \le |\,\delta_{\mathrm{I}}\,x_h\,| \qquad (h = 0, 1, \ldots, u)\,. \qquad [x_h\,,\,x_k]$$

In a completely analogous way, *the inequalities in Table 4 can be represented in the unified form:*

$$|\,\delta_{\mathrm{II}}\,y_h\,| \le |\,\delta_{\mathrm{I}}\,y_h\,| \qquad (h = 0, 1, \ldots, u)\,. \qquad [y_h\,,\,y_k]$$

We would like to derive the inequalities that are given in the tables from the relations (A), (B) [(A′), (B′), resp.] in that formulation.

Parameters $x_0\,, x_1\,, \ldots, x_n$.

Set:

$$\frac{\partial y_h}{\partial x_k} = p_{hk}\,, \tag{15}$$

to abbreviate. One will then have:

For Experiment I: $$\delta y_h = p_{hh}\,\delta_{\mathrm{I}}\,x_h\,, \tag{16}$$

For Experiment II: $$\begin{cases} \delta y_h = p_{hh}\,\delta_{\mathrm{II}} x_h + p_{hk} \delta_{\mathrm{II}} x_k\,, & (17) \\ \quad 0 = p_{kh}\,\delta_{\mathrm{II}} x_h + p_{kk} \delta_{\mathrm{II}} x_k\,. & (18) \end{cases}$$

In that way, δy_h is the "given change" in (16) and (17), and equation (18) formulates the requirement that one should have $\delta y_h = 0$ in Experiment II (i.e., x_k should be "left alone").

We will obtain the following relations between $\delta_{\mathrm{I}}\,x_h$ and $\delta_{\mathrm{II}}\,x_h$ from (16), (17), (18) when we eliminate δy_h and $\delta_{\mathrm{II}}\,x_k$ from them:

$$\delta_{\mathrm{II}}\,x_h \cdot (p_{hh}\,p_{kk} - p_{kh}\,p_{hk}) = p_{hh}\,p_{kk} \cdot \delta_{\mathrm{I}}\,x_h\,. \tag{19}$$

With the use of (B) and (C):

$$p_{hh}\,p_{kk} > 0\,, \tag{20}$$

$$p_{hh}\,p_{kk} = p_{hk}^2 = p_{kh}^2 > 0\,. \tag{21}$$

It will follow that:

$$|\,p_{hh}\,p_{kk} - p_{kh}\,p_{hk}\,| \leq |\,p_{hh}\,p_{kk}\,|\,, \tag{22}$$

moreover.

If we take the absolute values of both sides of equation (19) then that will imply the validity of the inequality $[x_h, x_k]$, when we consider the relation (22).

Parameters $y_0\,, y_1\,, \ldots, y_n$.

In a completely analogous way, when one employs the abbreviation:

$$\frac{\partial x_h}{\partial y_k} = q_{hk}\,, \tag{15$'$}$$

one will have:

For Experiment I: $$\delta x_h = q_{hh}\,\delta_{\mathrm{I}}\,y_h\,, \tag{16$'$}$$

For Experiment II: $$\begin{cases} \delta x_h = q_{hh}\,\delta_{\mathrm{II}} y_h + q_{hk} \delta_{\mathrm{II}} y_k\,, & (17') \\ \quad 0 = q_{kh}\,\delta_{\mathrm{II}} y_h + q_{kk} \delta_{\mathrm{II}} y_k\,, & (18') \end{cases}$$

$$\delta_{\mathrm{II}}\,y_h \cdot (q_{hh}\,q_{kk} - q_{kh}\,q_{hk}) = \delta_{\mathrm{I}}\,y_h \cdot q_{hh}\,q_{kk}\,. \tag{19$'$}$$

From (A′) and (B′), one has:

$$q_{hh}\, q_{kk} > 0\,, \tag{20′}$$

$$q_{hh}\, q_{kk} = q_{hk}^2 = q_{kh}^2 > 0\,, \tag{21′}$$

and therefore:

$$|\, q_{hh}\, q_{kk} - q_{kh}\, q_{hk} \,| \leq |\, q_{hh}\, q_{kk} \,|\,. \tag{22′}$$

If we take the absolute values of both sides of equation (19) and consider (22′) then we will verify the inequalities $[y_h, y_k]$.

Parameters $\eta_1, \ldots, \eta_t, x_{t+1}, \ldots x_{n+1}$.

Four combinations of (ρ, σ) are possible here: $[\eta_r, \eta_s]$, $[\eta_r, x_k]$, $[x_h, \eta_s]$, $[x_h, x_k]$. If we proceed here in precisely the same way that we did in the other two cases then we will easily obtain the desired inequalities from (A″) and (B″). However, we must now consider the fact that the right-hand and left-hand sides of the middle inequality in (B″) possess opposite signs. In that way, we will get the following inequalities for the four typical cases:

$$\begin{array}{ll} |\, \delta_{\mathrm{II}}\, \eta_r \,| \geq |\, \delta_{\mathrm{I}}\, \eta_r \,|\,, & [\eta_r, \eta_s]\,, \\ |\, \delta_{\mathrm{II}}\, \eta_r \,| \leq |\, \delta_{\mathrm{I}}\, \eta_r \,|\,, & [\eta_r, x_k]\,, \\ |\, \delta_{\mathrm{II}}\, x_h \,| \leq |\, \delta_{\mathrm{I}}\, x_h \,|\,, & [x_h, \eta_r]\,, \\ |\, \delta_{\mathrm{II}}\, x_h \,| \geq |\, \delta_{\mathrm{I}}\, x_h \,|\,, & [x_h, x_k]\,. \end{array}$$

The inequalities that belong to one of the "mixed" types (y, x), (x, y) *have the same signs as the inequality* (α) *in* § **1**.

However, the inequalities that belong to one of the "pure" types (y, y), (x, x) *have the opposite sign to the inequality* (α) *in* § **1**.

In the cases (y, y) and (x, y), the directly-affected parameter will show a higher capacity to resist in Experiment II, while in the cases (y, x) and (x, x), it will show a reduced capacity to resist (cf., the remarks following Table 2).

§ 11. Remarks concerning the practical application of the principle, on the one hand, and its formulation in lectures, on the other. – The results to which we arrived in §§ **2-5** seem to contradict the largely-undisputed fact that the **Le Chatelier-Braun** principle has quite often proved to be a useful guide for the teaching of *reciprocity effects:* Since the direction of the resulting inequality depends upon the random choice of the (ρ, σ) type and both directions of the inequalities already enter into the most common parameter system $(T, x_1, \ldots, x_n)$, one might often obtain the wrong sign in practical applications of the principle.

A remarkable observation will give us the solution to that apparent paradox: In the cases of *practical applications*, one never uses the principle in its abstract formulation, but one can only infer a certain type of comparison from it. *One solves the new cases by analogy with the old and well-known ones.* In that way, one *instinctively* juxtaposes the type (ρ, σ) in the new case being investigated with the analogous type (ρ, σ) of an already-known case, e.g. the type (T, x) with the same type (T, x). One never considers the *intuitive* conflict between y and x . In that way, one will get the correct sense of direction for the resulting inequality in the new case without fail and not once remark that it will change when one goes from one type (ρ, σ) to another. That is, in Experiment II, the old case, as well as the new one, will exhibit an *increased* "capacity to resist" in one case and an increased "adaptability" in the other, and both types of behavior cannot be given a common abstract formulation with no further analysis.

Things are completely different when it is precisely the abstract formulation that is at the forefront of interest, such as, e.g., in the theoretical treatment of the principle in a textbook or lecture: It will then seem that none of the known formulations of the principle really work. Neither the proof of the principle of action and reaction (**Nernst**), nor the plausibility of a "principle of the *most possible* conservation of the state" (**Weinstein**), nor the "accommodation capacity" (**Chwolson**) that are generally observed in nature will achieve that goal.

But is it even necessary to bother with a flawless formulation of that principle? In any event, one can achieve that only with *great* complexity when one, above all, separates intensity parameters from quantity parameters ([1]). However, when one has already made that decision, one can immediately introduce the reciprocity laws ([2]), which indeed express *quantitatively* what the **Le Chatelier-Braun** principle describes only *qualitatively* in the best of cases.

However, the meaning of this principle as the guiding principle for the experimental investigations of reciprocal effects and the corresponding education of our imagination perhaps lies, at least in part, in the flexibility of its formulation: If we are to make a *concrete, and for that reason fruitful, comparison* of each new case with a suitably-chosen old case then it will be necessary for us to resort to it, which could not happen with a consistent formulation of the principle. The true gist of the principle lies in the fact that each new (ρ, σ) case must actually always behave like the older (ρ, σ) case of the same type. For a long time now, the **Le Chatelier-Braun** principle has not been a rule that is applied like a template, but still leaves *one thing* to be discovered in each case: the true sign of the inequality!

([1]) In order to do that, one would, above all, allow only (y, y) or (x, x) types consistently. However, since x_0 (entropy, taken negatively) can hardly be chosen to be a state parameter, instead of y_0 (= T), as a rule, that would already recommend that one should consistently base (ρ, σ) upon the (y, y) type. One would thus come to the following formulation: Let a stable or indifferent equilibrium of a thermal system be established by the value of the (n + 1)-intensity parameter y_0 (= T). All y except y_h and y_k might be kept unconditionally constant. The quantity x_h that belongs to the intensity y_h is given a certain change δx_h . y_h is then the *directly-affected* intensity. In that way, the intensity y_k will be *fixed* the one time (Experiment I: $\delta y_k = 0$) and *left alone* the other time (Experiment II: $\delta x_h = 0$). The principle then states that one has, *without exception:*

$$| \delta_{\mathrm{II}}\, y_h | \geq | \delta_{\mathrm{I}}\, y_h | .$$

The physical sense of that inequality is a *raised* capacity to resist in the h^{th} degree of freedom in Experiment II. I mention that formulation only to show how complicated it proves to be.

([2]) One notes how simple the form is that they assume when one introduces the notations (13), (14); cf., (B) with (11).

Appendix

1. The distinction between intensity and quantity parameters y_h (x_h , resp.) that is so fundamental in thermodynamics requires an axiomatic treatment, perhaps in the way that **C. Caratheodory** ([1]) has recently contributed for the definition of other thermodynamic concepts.

2. The calculations that were developed in § **9** and § **10** can be adapted directly to the *electrodynamics of quasi-stationary currents*. The electromagnetic energy will then enter in place of u. The current strengths i_h are to be treated as intensities y_h , while the role of the x_h will be taken on by the corresponding "electro-kinetic moments" s_h . One will arrive at an analysis of **Lenz**'s law in that way. – In just the same way, one can go over to the reciprocity laws that **Helmholtz** defined for *cyclic systems* ([2]).

3. All of those developments rest upon the existence of corresponding potential functions. However, there also seem to exist *reciprocity effects that are essentially coupled with irreversible processes* (cf., some examples of them in the C. R. note of **Le Chatelier**). They can hardly be required by the existence of corresponding potential functions. For that reason, I have emphasized the fact that our methods of investigation are in no position to classify such reciprocity effects and give them a foundation with no further analysis.

St. Petersburg, the 8-21 April 1911.

([1]) Math. Ann. **67** (1909), 355-386, "Untersuchungen über die Grundlagen der Thermodynamik."

([2]) **Helmholtz**, "The physikalische Bedeutung des Prinzips der kleinsten Wirkung," § **4** in *Ges. Abh.* III, pp. 231. **Hertz**, *Mechanik*, § 568, *et seq.* (includes an error). **J. J. Thomson**, *Anwendung der Dynamik auf Physik und Chemie*, pp. 98, *et seq.*