

Stability, Displacement and Moderation of Chemical Equilibrium: Rediscovering Le Chatelier's Principle

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Abstract – Engineering education often makes reference to historical “laws” dating back to a time when science was still at an early stage of development. An example is the principle of displacement and moderation of chemical equilibrium formulated by Le Chatelier in various forms between 1884 and 1933. The principle was never given a proper mathematical form, and later workers restated it in increasingly ambiguous verbal terms, subject to doubtful or plainly wrong interpretations. We show by an examination of Le Chatelier's works that in fact he dismissed as incorrect the version usually associated nowadays with his name. His definitive formulation was much more specific, referring explicitly to changes in temperature, pressure and composition of a system. We compare this version with the predictions obtained from rigorous thermodynamic considerations. The results show that Le Chatelier's approved principle is also incorrect as a whole, but can be accepted as two separate statements, one for temperature and pressure changes in isolated systems, and the other for mass perturbations in isothermal, isobaric ideal mixtures. Finally, we reflect on the disadvantages of using unsound or “loose” versions of this principle in engineering education instead of a formal treatment.

Index Terms - Equilibrium, chemical reaction, Le Chatelier, stability, moderation.

INTRODUCTION

Recent papers [1-3] have drawn new attention to Le Chatelier's principle of displacement and moderation of chemical equilibrium. Lacy [1] has considered reactions that “shift left” upon addition of more reactant at constant temperature and pressure. Starting from the well known example of the ammonia reaction, $N_2 + 3H_2 = 2NH_3$, for which an addition of N_2 results in formation of more NH_3 only if the mole fraction of N_2 is less than $\frac{1}{2}$ (otherwise NH_3 decomposes), he has gone on to write general stoichiometric criteria for identifying reactions that may behave in this particular way. Uline and Corti [2] have noted that most discussions of such reactions assume ideal gas mixtures subject to infinitesimal perturbations, and have carried out a deeper analysis of the ammonia reaction to include the effects of gas phase nonidealities and finite changes in the amounts of each component. Martinez Torres [3] has

presented a thermodynamic treatment that leads to detailed rules for the reaction shifts that follow changes of intensive and extensive state variables, including component masses.

These works take different views of the validity of Le Chatelier's principle for the ammonia reaction: Reference [1] does not give a statement of the principle, but implies that this behavior complies with it and is unfamiliar only because it is seldom treated in textbooks, which deal mostly with changes at constant temperature and *volume* (for which the addition of a reactant *always* displaces the equilibrium towards the formation of more products); on the other hand, [2] presents it as an outright exception to the principle, stated as “in a system at equilibrium, a change in one of the variables that determines the equilibrium will shift the equilibrium in the direction counteracting the change in that variable”, and implicitly understood to include component mass among the determining variables. Lastly, [3] quotes the principle as “if a chemical system is subjected to a perturbation, the equilibrium will be shifted such as to partially undo this perturbation”, and notes that this ambiguous statement may support contradictory predictions, depending on whether the perturbation is interpreted to be “undone” by reducing the mass or the concentration of the reactant added.

It is the purpose of this contribution to point out that the notion that a chemical equilibrium shifts in the direction that consumes the mass of a component added to the system stems from an incorrect version of Le Chatelier's principle, which he himself rejected. We then analyze the statement that Le Chatelier sanctioned, and show that it contains two functionally unrelated but separately valid assertions, one true only for isolated systems, and the other true only for isothermal isobaric systems.

LE CHATELIER'S PRINCIPLES

The example of the ammonia reaction has been known since Le Chatelier's time. Some accounts [4-6] trace it back to the work of Posthumus in 1933, but Le Chatelier himself [7] acknowledged that the “difficulty” had been signaled by Ariès in a treatise on thermodynamics published in 1904. Whether this behavior constitutes an exception to, or violation of, Le Chatelier's principle depends in fact on which of the many versions of the principle is being questioned. A brief account of the early history of the principle may be instructive in this respect.

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Le Chatelier's original statement appeared in 1884 as [8, 9] "every system in stable chemical equilibrium, subjected to the influence of an external cause which tends to change either its temperature or its condensation (pressure, concentration, number of molecules in unit volume), either as a whole or in some of its parts, can only undergo such internal modifications as would, if produced alone, bring about a change of temperature or of condensation of opposite sign to that resulting from the external cause". If "condensation" is taken to include mole fractions, then the (ideal-gas) ammonia reaction conforms to this statement, because if the mole fraction x_{N_2} is greater than $\frac{1}{2}$, it actually increases as nitrogen is consumed [4, 5, 7, 10, 11].

By 1888, however, Le Chatelier's intricate but very specific first formulation had become more generalized [9, 12]: "Any system in equilibrium experiences, upon variation of a single one of the equilibrium factors, a transformation in the direction that would, if it occurred alone, bring about a change of the opposite sign in the factor under consideration". Identification of the "equilibrium factors" has been a matter of controversy ever since. From a later presentation [13] we learn however that "the only conditions whose variation may alter the equilibrium state of a chemical system are those whose variation demands the expenditure of motive power". These are the "determining conditions of chemical equilibrium", the list of which includes "physical state, condensation, temperature, pressure, electromotive force, magnetic intensity, etc". The principle is now given as "any change in one of the determining conditions of equilibrium produces a chemical transformation of the system that tends to cause a variation of the opposite sense in the condition under consideration". The phrasing of this sentence is contradicted however by examples where "any rise in the temperature of a system currently in equilibrium will produce a reaction that absorbs heat" [not one that *lowers the temperature*] and "any rise in pressure [will produce] a reaction that diminishes the volume" [not *the pressure*]. The case of mass changes is not discussed.

It appears that Le Chatelier perceived the "conditions" of equilibrium as consisting of pairs of functionally equivalent conjugate variables (e.g. pressure – volume), one measuring the external perturbation and the other the internal displacement. In effect, in a textbook published in 1926 [14], after considering variations in the temperature, pressure and electromotive force, he gave the respective formulas $SdT > 0$, $VdP < 0$ and $IdE < 0$, and stated that "a rise in temperature provokes a reaction that tends to produce a decrease in temperature, that is a reaction that absorbs heat. An increase in pressure produces a reaction that tends to bring about a decrease in pressure, that is a reaction that diminishes volume, and the same [is true] for electricity". He muddled the issue, however, by stating the law this time as "the modification of any of the conditions that influence the state of chemical equilibrium of a system of species, provokes a reaction in the direction that tends to generate a change of the opposite sense of the external condition [la condition extérieure] modified" (i.e. the system response now seeks to modify the conditions of the surroundings), and observing that "this same law is also exact for mass actions: the increase in a homogeneous system of the mass of one of the

species in equilibrium provokes a reaction that tends to decrease the mass of the same species" (which is not, of course, *external* to the system).

In 1933, when Le Chatelier finally confronted the need to explain the "difficult" behavior of the ammonia reaction, he came to realize [7] that his different statements of the law of displacement of equilibrium were not all equivalent, as he had thought. Rather, "some of them are inexact, and those are precisely the ones that have been more generally adopted". The problem, he warned, lay only in the effect of mass changes, because as concerned the other factors (temperature, pressure and electromotive force) the principle was firmly grounded on the two laws of thermodynamics. Stating now that "concentration" meant "the number of molecules of a species in one molecule of total mixture", i.e. mole fraction, he used a generic reaction $\alpha A + \beta B = \gamma C + \delta D$ to show that addition of a small amount of A always increases its concentration, but formation of A by chemical reaction may increase or decrease it, depending on the stoichiometric coefficients α , β , γ , δ . He gallantly admitted that *while his first (1884) statement of the law was correct, his seemingly equivalent second (1888) statement was not*. His error, he said, had been to believe that an increase of mass always implied an increase of concentration. The correct statement should be: "In a homogeneous mixture in chemical equilibrium, an increase in the concentration of one of the reacting components displaces the equilibrium in the direction in which the reaction tends to decrease the concentration of the same species".

It must be noted that Le Chatelier did not prove this final statement; he believed in the existence of a law of moderation, and reasoned that if mass was not the correct factor, then it must be "concentration", which appeared to move in the correct direction. In a subsequent note [15] he showed that for ideal mixtures the effect of concentration changes was equivalent to the performance of external work. Shortly afterwards, he also introduced to the Académie des Sciences a paper by Étienne [16] that proved, from rigorous thermodynamic stability considerations, that for ideal mixtures the reaction shift is ruled by the equation

$$\left(\frac{\sum \nu_k}{\sum N_k} - \frac{\nu_i}{N_i} \right) \delta N_i \delta \xi < 0 \quad (1)$$

where N_i are the moles, ν_i are the stoichiometric coefficients (positive for products, negative for reactants, zero for inert species), and ξ is the degree of reaction, taken to increase as the reaction proceeds "to the right", i.e. as reactants convert to products. Equation (1) has been rediscovered many times in the literature on the subject.

Unfortunately, Le Chatelier's retraction went largely unnoticed. As he lamented, it was the flawed 1888 formulation that gained widespread acceptance and in time led to increasingly broader and hazier formulations in terms of "stresses" or "disturbances". Not surprisingly, such versions of the principle have been the source of many misconceptions, misunderstandings and misinterpretations [6, 11, 17-23]. No such confusion should exist however in the particular case of mass perturbations, where it is clear

from the above that *it is doubly incorrect to assert (and teach) that Le Chatelier's principle predicts that an increase in the amount of one component shifts the equilibrium in the direction that decreases the mass of that component*, because such prediction is neither universally true nor Le Chatelier's, having been disproved and disowned by him.

FROM GIBBS TO LE CHATELIER

It was none other than Le Chatelier who first translated Gibbs' *On the equilibrium of heterogeneous substances* [24] into French. In his preface [25], Le Chatelier commented on the many new concepts and laws contributed by Gibbs, including the "law of stability of chemical equilibrium", which in his opinion "had gone completely unnoticed [...] although *it was formulated there more completely than ever since*" (italics ours). He even pointed to what he considered the relevant pages, but could not resist giving his own statement of the law, "any change in one of the equilibrium factors: pressure, temperature, concentration, induces a transformation of the system that tends to produce a change of the opposite sign in the factor under consideration", neither proved nor even implied in the pages he cited [26].

The validity of Le Chatelier's sanctioned version of his principle should therefore be examined in the framework of Gibbs' thermodynamic theory of equilibrium and stability of multicomponent systems. Many treatments are available in the literature that address this problem at varying levels of complexity, including different sets of constraints, mixture nonidealities, finite changes, and multiple reactions, e.g. [3-5, 11, 16, 27-39]; the list is not exhaustive. From these, correct "principles" can be extracted for the displacement and moderation of chemical reactions. The following summary presentation is limited to the basic elements that may help in assessing the ultimate validity and pertinence of Le Chatelier's principle. The development follows [36] and is similar to that recently presented in [3].

We must surely equate the "factors" or "determining conditions" of equilibrium with the independent variables that determine the thermodynamic state of a reactive system, and whose perturbation by external manipulation therefore alters this state. These must be taken from conjugate pairs of extensive and intensive properties representing thermal (entropy S , temperature T), mechanical (volume V , pressure P) and chemical (mass or moles N_i , potentials μ_i) contributions to the system energy. These are the *only* sets possible; no fundamental thermodynamic equation exists in terms e.g. of P and V as independent variables. Different combinations imply different energy representations; the classical fundamental functions are internal energy U , enthalpy H , Helmholtz energy A and Gibbs energy G , such that

$$\begin{aligned} dU - TdS + PdV &= dH - TdS - VdP = \\ dA + SdT + PdV &= dG + SdT - VdP = \sum \mu_i dN_i \end{aligned} \quad (2)$$

As can be seen, these functions differ in their thermal and mechanical independent variables, although the chemical independent variables are always the moles N_i . This leads to a crucial difference when the stability of equilibrium states is

considered. Internal energy, which depends wholly on extensive variables (S, V, N_1, \dots, N_n) must be a *minimum with respect to all of them*. The other energy functions depend on at least one of the intensive variables T, P (which switch roles with their conjugate variables S, V by Legendre transformation) and must be a *minimum with respect to the extensive variables*, but a *maximum with respect to the intensive ones* [24, 40],

$$\begin{aligned} d^2U &> 0 \\ (d^2H)_P &> 0, \quad (d^2H)_{S, N_1, \dots, N_n} < 0 \\ (d^2A)_T &> 0, \quad (d^2A)_{V, N_1, \dots, N_n} < 0 \\ (d^2G)_{T, P} &> 0, \quad (d^2G)_{N_1, \dots, N_n} < 0 \end{aligned} \quad (3)$$

We consider for generality an energy function $E(X_1, \dots, X_{n+2})$ where X_1, X_2 are the thermal and mechanical independent variables and $X_{i+2} = N_i$. In a closed reactive system, the component moles do not change independently but in fixed stoichiometric proportions, and thus can be expressed in terms of the single variable ξ as

$$dN_i = \nu_i d\xi \quad (4)$$

Therefore, the minimum energy criterion

$$(dE)_{X_1, X_2} = (\sum \nu_i \mu_i) d\xi = 0 \quad (5)$$

leads in all representations to the same condition for chemical equilibrium

$$\Delta\mu \equiv \sum \nu_i \mu_i = 0 \quad (6)$$

The quantity $\Delta\mu$ in (6) represents the differential energy change per unit extent of reaction; its negative is known as the *affinity* of the reaction. One can easily infer from (5) the direction in which the reaction will proceed when not in equilibrium, e.g. if $\Delta\mu > 0$ the reaction must shift "left" because $d\xi < 0$ gives $dE < 0$.

Before continuing with the analysis, it is instructive to examine (6) from a purely logical perspective. Clearly, *any change in the system conditions alters the equilibrium only if it changes the chemical potentials so that (6) is no longer satisfied*. Whatever the factors of equilibrium, the actual perturbation comes from their effect on the μ_i . Conversely, *the response to a perturbation is to change the μ_i so that (6) is restored*. This is accomplished by changing the extent of reaction, i.e. the component masses. In particular, a change in the amount of the components is significant only if it changes the system composition and therefore the μ_i . Doubling, say, the moles of *every* component present has no effect on the intensive properties and does not qualify as a perturbation. Changing the amount of a component present as a pure phase (e.g. a solid) would also be inconsequential [16]. By contrast, changing the amount of an *inert* component does change the composition of a mixture and therefore disturbs and displaces the equilibrium. If the

amount of the inert species were the “stress”, no shift in the reaction would be possible to counteract it.

With the system in an equilibrium state given by (6), an infinitesimal perturbation is now introduced in one of the X_i . The effect of this “action” on (6) is

$$\delta_{axn}(\Delta\mu) = \left(\frac{\partial Y_i}{\partial \xi} \right)_{X_1, X_2} \delta_{axn} X_i \quad (7)$$

where Y_i is the conjugate variable for X_i .

Equilibrium is next restored by the spontaneous system “reaction” at the new (perturbed) conditions to give

$$\delta_{rxn}(\Delta\mu) = \left(\frac{\partial^2 E}{\partial \xi^2} \right)_{X_1, X_2} \delta_{rxn} \xi \quad (8)$$

The second derivative in the r.h.s. of (8) involves only mass changes and must be positive by (3). On summing (7) and (8) to zero, the general displacement formula is obtained:

$$(\delta_{axn} X_i)(\delta_{rxn} Y_i) = - \left(\frac{\partial^2 E}{\partial \xi^2} \right)_{X_1, X_2} (\delta_{rxn} \xi)^2 < 0 \quad (9)$$

which can be stated as: *The perturbation of an independent variable displaces the equilibrium in the direction that produces a change of the opposite sign in the corresponding conjugate variable* [3, 5, 35, 36]. It makes no difference whether the perturbed variable is an intensive or an extensive property. In particular, for mass perturbations we conclude at once that *a change in the mass of one component displaces the equilibrium in the direction that produces a change of the opposite sign in the chemical potential of the same component*, irrespective of the identity of the component (reactant, product or inert), the nature of the system (ideal or nonideal), or the thermal (S or T) and mechanical (V or P) properties held constant. This is the correct statement on mass disturbances that Le Chatelier never managed to formulate and some other later workers similarly missed.

It is also of interest to examine the indirect effect of the perturbation $\delta_{axn} X_i$ on the corresponding conjugate variable,

$$\delta_{axn} Y_i = \left(\frac{\partial Y_i}{\partial X_i} \right)_{X_{k \neq i}} \delta_{axn} X_i \quad (10)$$

The second order differentials in (3) are quadratic forms whose positive- or negative-definiteness imposes well known conditions on the partial derivatives of the energy function. Specifically, the main diagonal elements must be

$$\left(\frac{\partial Y_i}{\partial X_i} \right)_{X_{k \neq i}} \begin{cases} > 0 & \text{intensive } Y_i \\ < 0 & \text{extensive } Y_i \end{cases} \quad (11)$$

From (9)–(11) follows the general displacement formula:

$$(\delta_{axn} Y_i)(\delta_{rxn} Y_i) \begin{cases} < 0 & \text{intensive } Y_i \\ > 0 & \text{extensive } Y_i \end{cases} \quad (12)$$

which can be stated as: *The indirect perturbation of an extensive variable displaces the equilibrium in the direction that reduces the change in the corresponding conjugate intensive variable. On the contrary, the indirect perturbation of an intensive variable displaces the equilibrium in the direction that amplifies the change in the corresponding conjugate extensive variable* [3-5, 35, 36]. In particular, for a perturbation in the amount of one component (12) becomes

$$(\delta_{axn} \mu_i)(\delta_{rxn} \mu_i) < 0 \quad (13)$$

i.e. moderation is expressed not in terms of mass but of its conjugate variable, chemical potential. In fact, *there is no possible statement of moderation in terms of masses in any energy representation*, because none of the fundamental functions involve these as dependent variables.

The above results do not indicate whether the reaction actually shifts “right” or “left” as a result of a perturbation. On rewriting (9) as

$$\left(\frac{\partial \xi}{\partial X_i} \right)_{X_{k \neq i}} = - \frac{(\partial Y_i / \partial \xi)_{X_1, X_2}}{(\partial^2 E / \partial \xi^2)_{X_1, X_2}} \quad (14)$$

we see that the sign of $d\xi$ depends on the numerator of (14), i.e. on the properties of each specific system, and cannot be predicted universally.

It is fairly straightforward to compile specific versions of the above formulas for each energy function and type of perturbation. These are not presented here because of space limitations, but a set of tables is available from the authors on request.

We are now in a position to analyze Le Chatelier's final and definitive statement of his principle. Consider first the effect of thermal and mechanical perturbations, for which he maintained his 1884 formulation. As he referred to changes in temperature and pressure, which are the independent variables of the Gibbs energy function, we use (9) to obtain

$$\begin{aligned} (\delta_{axn} T)_{P, N_1, \dots, N_n} (\delta_{rxn} S)_{T, P} &> 0 \\ (\delta_{axn} P)_{T, N_1, \dots, N_n} (\delta_{rxn} V)_{T, P} &< 0 \end{aligned} \quad (15)$$

e.g. an increase in temperature displaces the equilibrium in the direction that increases the system entropy, and an increase in pressure displaces the equilibrium in the direction that decreases the system volume. Unfortunately, whether these displacements would, if produced alone, bring about respective decreases in temperature and pressure cannot be ascertained, because the processes by which they might do so are undefined unless further constraints are specified. For example, an increase in the system entropy at constant pressure and composition would *increase* its temperature, and a decrease in the system volume at constant temperature and composition would similarly *increase* its pressure, exactly the opposite of Le Chatelier's statement. The

problem is of course that if T and P are the independent variables, the statements of moderation do not involve these but their conjugates $-S$ and V , and the most we can get from (12) is

$$\begin{aligned} (\delta_{axn}S)_{P,N_1,\dots,N_n} (\delta_{rxn}S)_{T,P} &> 0 \\ (\delta_{axn}V)_{T,N_1,\dots,N_n} (\delta_{rxn}V)_{T,P} &> 0 \end{aligned} \quad (16)$$

i.e. neither entropy nor volume changes (being extensive variables) are moderated.

A plausible alternative is suggested by Le Chatelier's exact wording of his 1884 principle, and also by his acknowledged indebtedness to Gibbs. If the temperature and pressure changes result from the influence of an external cause, it may be that T and $-P$ are in fact the *dependent* variables, conjugate to the actually manipulated variables S and V in the internal energy representation. From (12) we obtain then at once

$$\begin{aligned} (\delta_{axn}T)_{S,N_1,\dots,N_n} (\delta_{rxn}T)_{S,V} &< 0 \\ (\delta_{axn}P)_{S,N_1,\dots,N_n} (\delta_{rxn}P)_{S,V} &< 0 \end{aligned} \quad (17)$$

which coincides with Le Chatelier's statement. Thus, Le Chatelier's approved version of his principle is correct *only for perturbations in the internal energy representation* (the only one that contains both T and P as *dependent* variables), i.e. temperature changes induced by altering the system entropy (at constant volume), pressure changes induced by altering the system volume (at constant entropy), and the subsequent reaction taking place under conditions of total isolation (adiabatic, rigid, impermeable walls).

Consider now the effect of mass perturbations. The correct result is of course (13), valid for all energy representations. Here it seems fair to limit the discussion to ideal systems, given that theories of nonideal solutions had hardly been developed in Le Chatelier's time. For an ideal mixture,

$$\mu_i = g_i(T,P) + RT \ln x_i \quad (18)$$

and (13) becomes

$$(\delta_{axn}x_i)_{T,P} (\delta_{rxn}x_i)_{T,P} < 0 \quad (19)$$

but in this case *only for perturbations in the Gibbs energy representation*. In any other case, including the internal energy function, extra terms would arise from the derivatives of the pure component energy g_i .

In conclusion, therefore, Le Chatelier's final statement is not valid as a whole, but should be separated in two unrelated parts, one concerning thermal and mechanical perturbations in an isolated system, the other concerning mass perturbations in an isothermal, isobaric system.

We close this analysis by noting that, for ideal mixtures, (14) can be written as

$$\left(\frac{\partial \xi}{\partial N_i} \right)_{T,P,N_{k \neq i}} = -RT \frac{(\partial \ln x_i / \partial \xi)_{T,P}}{(\partial^2 G / \partial \xi^2)_{T,P}} \quad (20)$$

This can be shown to lead directly to (1). The behavior of the ammonia reaction, among others, is thus perceived as a *corollary*, not a violation, of a correctly stated Le Chatelier's principle.

COMMENTS AND CONCLUSIONS

We have shown that the statement traditionally associated with Le Chatelier's name was actually rejected by him in favor of a corrected version of his very first formulation. We have presented rigorous equations of displacement and moderation of chemical equilibria, and used them to establish that Le Chatelier's definitive version of his principle is also invalid as a whole, because it mixes two different energy representations. However, the statements on thermal and mechanical perturbations of isolated systems, and mass perturbations of isothermal, isobaric systems can be accepted by separate. This is indeed the ambiguity and the source of confusion in Le Chatelier's principle, that he never made clear the constraints and conditions for which his formulations were intended.

The general "principles" embodied by (9) and (12) are much more specific than Le Chatelier's pronouncements. They are also less appealing, because they do not claim to represent some fundamental law of nature (just very specific conducts of chemical systems), and more difficult to present at an early stage of engineering education, because of the thermodynamic background required. In the absence of these basic elements, there seems to be little if any advantage in teaching a "light" version of Le Chatelier's principle that lacks theoretical foundation and can create persistent misconceptions. In fact, the principle's predictions are essentially qualitative, and can perfectly well be obtained from actual computations of chemical equilibria. We see the main value of the principle as an illustration of the behavior of systems in stable equilibrium, pertaining therefore to advanced courses in thermodynamics or physical chemistry.

In his application of Le Chatelier's principle to theoretical economics, Nobel prizewinner Paul A. Samuelson [41, 42] found it necessary to replace the usual "vague" and "teleological" principle by an unambiguous mathematical formulation derived from the properties of convex functions and positive definite quadratic forms. It is worth mentioning that he traced his interest in the subject back to the teachings of Edward B. Wilson, who had been the last student of Gibbs at Yale. To Le Chatelier's avowed preference [14] "to give a very simple general statement of this law, without using any algebraic formulas", Samuelson [43] opposed Gibbs' dictum that "mathematics is a language". That we in engineering education should feel exempt from this same need, especially clinging instead to a statement that Le Chatelier himself recanted is surely the main remaining contradiction associated with this principle.

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