

# THE PRINCIPLE OF LE CHATELIER AND BRAUN

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IN THE discussion of chemical equilibria nearly all textbooks of general chemistry and most textbooks of physical chemistry adapt a *principle of moderation* which may be expressed as follows:

*If a chemical system in equilibrium is subjected to a perturbation (stress), the equilibrium will be shifted (a reaction will occur) such as to partially undo this perturbation (oppose the stress).—(I)*

This principle can be traced back to A. L. Le Chatelier (1) and F. Braun (2a, 2b). Le Chatelier acknowledges that he was inspired by the more restricted *principle of mobile equilibrium* of J. H. van't Hoff (3) (see the closing paragraphs of this article), and by G. Lippmann's ideas in the field of electricity (4). In turn, Lippmann refers to Lenz and his famous law (5):

When a force acting on a primary electric current induces a secondary current, the direction of the latter is such that its electrodynamical action opposes the acting force.

The Le Chatelier-Braun principle made a great impact on the chemistry of the turn of the century, and the possibility of numerous applications gave it a popularity which has persisted to the present. As early as 1909, however, P. Ehrenfest (6) and M. C. Raveau (7) pointed out that this principle in the form (I), or in any form equivalent to (I), is vague and ambiguous. Ehrenfest's 1911 paper is a true masterpiece; not only does he show flaws in a "proof" given by Braun (2b) (Le Chatelier never gave a theoretical justification), but he is also the first one to emphasize that a more careful formulation on the basis of thermodynamics clearly suggests two sets of cases: Under certain conditions the systems will indeed *oppose* a perturbation, (they are capable of resistance, "widerstandfähig,") but under other conditions they will *relieve* the perturbation (they are capable of adaptation, "anpassungsfähig"). In the last decades several chemists and physicists have rephrased and supplemented Ehrenfest's remarks (references in subsequent paragraphs), but their efforts have remained surprisingly unnoticed. Thus we find in the mind of many scientists the false notion that the Le Chatelier-Braun principle is "true" in the sense that it expresses some fundamental law of nature, the validity of which cannot be questioned. For example, in a leading monograph of the twenties we find (8):

No proof (. . . of the Le C.-B. principle . . .) in the ordinary sense can be given; it is a generalization based on experience.

And in one of the outstanding modern textbooks of physical chemistry we read (9):

This (. . . the Le C.-B. principle . . .) is a principle of broad and general utility, and it can be applied not only to chemical equilibria, but to equilibrium states in any physical system. It

is indeed possible that it can be applied also with good success in the psychological, economic, and sociological fields.

In view of these and other far-reaching claims by physical chemists, and the blind acceptance of the principle in a formulation such as (I) above in general and inorganic chemistry, we feel justified in submitting a critical discussion, on a solid thermodynamical basis, to THIS JOURNAL.

## QUALITATIVE DISCUSSION

Suppose that a gas reaction has come to equilibrium at a certain pressure  $P$  and temperature  $T$ . We introduce the "perturbation" by placing this mixture in a thermostat at temperature  $T + \delta T$ , maintaining the pressure at  $P$ . Then in due time our reaction mixture will have to adopt the new temperature  $T + \delta T$ , and no chemical reaction or any other change can ever "oppose" or even partially "undo" this. Thus, taken literally, formulation (I) is nonsense.

It is possible however to phrase a meaningful and interesting question. To understand this clearly, let us assume for the moment that we could prevent any reaction from taking place in our gas mixture, i.e., "freeze the equilibrium." Then, in acquiring the new equilibrium temperature, an amount of heat,  $q_0$ , would be absorbed by the system from the thermostat. But, of course, in reality a chemical reaction *does* take place, and with it is associated a certain heat effect. Consequently, when thermal equilibrium is established, the gas mixture will have taken up an amount of heat from the thermostat,  $q$ , which is not equal to  $q_0$ . The relevant question is whether  $q$  is larger than or smaller than  $q_0$ . As we shall see in later portions of the discussion, the correct answer is:

$$q > q_0 \quad (1)$$

In words: The temperature increase induces an endothermic reaction to take place, so that *more* heat is taken up from the thermostat than would have been the case if all gases had been inert. Thus the equilibrium shift does not "oppose" the heat transfer; to the contrary, it "aids" it.

As our second example we consider a gas mixture under adiabatic conditions. We impose a perturbation by increasing the volume from  $V$  to  $V + \delta V$ . Again, no process can ever take place in the reaction mixture which can "oppose" this volume increase. The correct question to ask here is whether on account of an induced chemical reaction the actual pressure lowering,  $|\delta P|$ , is larger than or smaller than the pressure lowering,  $|\delta P_0|$ , which would accompany the volume increase if all gases were inert. As we shall derive later, the answer is:

$$|\delta P| < |\delta P_0| \quad (2)$$

The reaction indeed, in this indirect way, "opposes" the volume change.

These two examples clearly show the dichotomy already observed by Ehrenfest. Thirdly, as a slightly different type of an example, we consider the reaction:



at constant temperature. We ask what will happen if we add  $\text{N}_2$  to an equilibrium mixture. The Le Chatelier-Braun principle, as expressed by (I) above, tells us that some  $\text{NH}_3$  will be formed in order to take away the added component and partially "undo" the change. But the correct answer is: What will happen depends entirely on the initial composition of the mixture and the conditions under which the  $\text{N}_2$  is added. We shall see later that if the original mixture contains more than 50 mole %  $\text{N}_2$ , the addition, if made at constant total pressure, will lead to the decomposition of some  $\text{NH}_3$  under the formation of even more  $\text{N}_2$ . If however, under similar conditions, we add  $\text{N}_2$  to an equilibrium mixture containing less than 50 mole % of this gas, the result will be the formation of some  $\text{NH}_3$ . Thus the situation is very complex indeed.

The problem, to enunciate a clear and unambiguous principle, which may be derived rigorously on the basis of thermodynamics and which covers all possible cases, has been tackled in a variety of ways by several authors (6, 10-16). In our opinion, the most elegant discussion, leading directly to a very general and abstract formulation, has been given by Epstein (14). Since we address ourselves primarily to chemists, we prefer to give the derivation for a special case involving a specific chemical reaction equilibrium. Subsequently we shall write down the generalization without proof. In the course of this analysis, equations (1) and (2) will appear in a slightly modified form. We shall return to the ammonia formation and show how the newly obtained rule may be applied to this case. In two final sections we shall make a comparison with van't Hoff's principle of mobile equilibrium and draw some general conclusions. Before embarking upon this sequence, however, we wish to summarize briefly certain basic thermodynamic formulas in a form with which many physical chemists, in particular in the U. S. A., are still unfamiliar.

#### BASIC THERMODYNAMIC FORMULAS; DEGREE OF ADVANCEMENT AND AFFINITY OF A CHEMICAL REACTION

The formulation of certain basic laws of thermodynamics in terms of the notions "affinity" and "degree of advancement" of a chemical reaction are due to Th. de Donder and his school (17, 18). It may be mentioned here that within the last decade the "Thermodynamics of Irreversible Processes" has made its impact, and since this new branch of physical science employs the de Donder system, the latter is beginning to receive some attention in this country (19).<sup>1</sup>

<sup>1</sup> Prigogine not only offers a clear and concise introduction to this subject of growing importance (which otherwise lies beyond the scope of this paper), but the introductory chapters also give an excellent summary of the de Donder formulation of "ordinary" thermodynamics.

We start with the fundamental Gibbs equation for closed multicomponent systems:

$$dE = TdS - PdV + \sum_i \mu_i dn_i \quad (3)$$

or

$$dS = (1/T)dE + (P/T)dV - (1/T) \sum_i \mu_i dn_i \quad (4)$$

where the  $\mu_i$  are the chemical potentials and the  $n_i$  the mole numbers of the various constituents  $i$ . Introduce the Gibbs free energy,  $G$ , and the Helmholtz free energy (work function),  $F$ :<sup>2</sup>

$$G = E - TS + PV \quad (5)$$

$$F = E - TS \quad (6)$$

By combination of (3) with (5) and (6), respectively, we obtain:

$$dG = -SdT + VdP + \sum_i \mu_i dn_i \quad (7)$$

and

$$dF = -SdT - PdV + \sum_i \mu_i dn_i \quad (8)$$

Next let us allow for a chemical reaction between the components, the equation for which we shall write as:

$$\sum_i \nu_i a_i = 0 \quad (9)$$

Here the  $\nu_i$  are the stoichiometric coefficients and the  $a_i$  the molar quantities of the corresponding substances. In using (9) we shall adopt the convention that the  $\nu_i$  are to be taken positive when  $i$  appears on the right, and negative when  $i$  appears in the left of the reaction equation in its more common form, with the "reactants" on the left and the "products" on the right. Now introduce the "degree of advancement" of the reaction,  $\xi$ , by the definition:

$$dn_i = \nu_i d\xi \quad (10)$$

Obviously this equation, which holds for each  $i$ , does not fix an absolute value of  $\xi$ , unless some initial conditions are specified. To eliminate all arbitrariness, we shall assume that at time  $t = 0$  we have exclusively "reactants" and set  $\xi$  equal to zero at this instant. As the reaction sets in,  $\xi$  increases to its equilibrium value  $\xi_e$ . If the reactants could be completely converted into products,  $\xi$  would attain its maximum value of unity.<sup>3</sup>

Next we define the "affinity" of the reaction,  $A$ , by

$$A = - \sum_i \nu_i \mu_i \quad (11)$$

For a given reaction  $A$  is not only a function of the usual state variables, but also of  $\xi$ , as are the  $\mu_i$ .<sup>4</sup>

<sup>2</sup> We use  $G$  and  $F$ , rather than  $F$  and  $A$ , for the free energy functions, since we shall use the letter  $A$  for "Affinity."

<sup>3</sup>  $\xi$ , as defined, is related to the chemical reaction rate by  $v = d\xi/dt$ .

<sup>4</sup> In MARK W. ZEMANSKY'S "Heat and Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1951, the affinity is

defined as  $A_{1/2} = \sum_i \nu_i(\mu_i)\xi = 1/2$ . Of course  $A_{1/2}$  is a constant.

With (10) and (11), the equations (3), (4), (7), and (8) can be written as follows:

$$dE = TdS - PdV - Ad\xi \quad (12)$$

$$dS = (1/T)dE + (P/T)dV + (A/T)d\xi \quad (13)$$

$$dG = -SdT + VdP - Ad\xi \quad (14)$$

$$dF = -SdT - PdV - Ad\xi \quad (15)$$

From (12), (14), and (15) we obtain alternative definitions of  $A$ :

$$A = -(\partial E/\partial \xi)_{S, V} = -(\partial G/\partial \xi)_{P, T} = -(\partial F/\partial \xi)_{V, T} \quad (16)$$

Hence in order to know  $A$ , we have to know  $E$ ,  $G$ , or  $F$ , (depending on the general reaction conditions) as a function of  $\xi$ . As an example we have drawn in Figure 1 a typical plot of  $G_{P, T}$  versus  $\xi$  and in Figure 2 we show the corresponding variation of  $A$ . For the equilibrium mixture  $G_{P, T}$  is a minimum and  $A$  is zero. As  $\xi$  increases,  $A$  goes from  $+\infty$  through the equilibrium value to  $-\infty$ . Note that for all  $\xi$ :

$$(\partial A/\partial \xi)_{P, T} < 0 \quad (17)$$

For a detailed discussion of affinity we refer to the literature (15, 16, 17, 18). For our purpose it is important to mention that the general appearance of the  $A$  vs.  $\xi$  curve, as shown in Figure 2, is preserved when the auxiliary conditions are different. Thus we have for reactions at constant  $V$  and  $T$ :

$$(\partial A/\partial \xi)_{V, T} < 0 \quad (18)$$

and for a process in an isolated system (adiabatic and at constant  $V$ ):

$$(\partial A/\partial \xi)_{S, V} < 0 \quad (19)$$

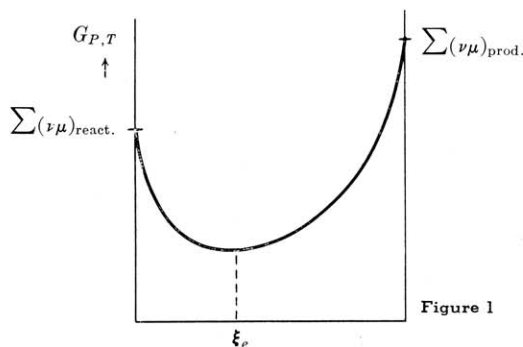


Figure 1

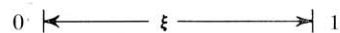


Figure 2

## RIGOROUS THERMODYNAMIC DERIVATION

We return to the second example of the qualitative discussion and consider the adiabatic volume increase of a mixture of reacting gases. We are now in a position to write down the implied result (2) in a more explicit form as follows:

$$-(\partial P/\partial V)_{S, A} \cdot \delta V < -(\partial P/\partial V)_{S, \xi} \cdot \delta V \quad (20)$$

The term on the right gives the pressure lowering which would result if no reaction could take place ( $\xi$  constant). The term on the left gives the pressure lowering accompanying the equilibrium shift ( $A$  remains constant at zero). Of course, both sides of (20) are positive. We shall now proceed to prove equation (20) (15).

Since we have an adiabatic process,  $P$  may be written as a function of  $V$  and  $\xi$ :

$$dP = (\partial P/\partial V)_{S, \xi} dV + (\partial P/\partial \xi)_{S, V} d\xi$$

from which:

$$-(\partial P/\partial V)_{S, A} = -(\partial P/\partial V)_{S, \xi} - (\partial P/\partial \xi)_{S, V} \cdot (\partial \xi/\partial V)_{S, A} \quad (21)$$

But since  $A$  is also a function of  $V$  and  $\xi$ :

$$dA = (\partial A/\partial V)_{S, \xi} dV + (\partial A/\partial \xi)_{S, V} d\xi$$

from which:

$$(\partial \xi/\partial V)_{S, A} = -[(\partial A/\partial V)_{S, \xi}]/[(\partial A/\partial \xi)_{S, V}] \quad (22)$$

Finally, from (12), since  $dE$  is an exact differential:

$$(\partial P/\partial \xi)_{S, V} = (\partial A/\partial V)_{S, \xi} \quad (23)$$

Upon substitution of (23) and (22) in (21) we obtain:

$$-(\partial P/\partial V)_{S, A} = -(\partial P/\partial V)_{S, \xi} + [(\partial A/\partial V)_{S, \xi}]^2/[(\partial A/\partial \xi)_{S, V}] \quad (24)$$

The term on the left of (24) is positive and so is the first term on the right. But the last term on the right is negative, since the denominator is negative by (19). Hence:

$$-(\partial P/\partial V)_{S, A} < -(\partial P/\partial V)_{S, \xi} \quad (25)$$

which completes the proof of (20). At the same time (25) implies:

$$-(\partial V/\partial P)_{S, A} > -(\partial V/\partial P)_{S, \xi}$$

hence:

$$-(\partial V/\partial P)_{S, A} \cdot \delta P > -(\partial V/\partial P)_{S, \xi} \cdot \delta P \quad (26)$$

Thus, whereas (20) shows that our system "resists" volume changes, at the same time (26) shows that it "relieves" pressure changes, and the Ehrenfest dichotomy appears directly within the framework of our derivation.

## GENERALIZATION; FORMULATION OF A VALID PRINCIPLE

Generalized treatments may be given along essentially the same lines as suggested in the previous section (10, 11, 14, 15). In order to formulate the results in the most elegant way, we write equations (3) or (12) in the form:

$$dE = \sum_j X_j dx_j \quad (27)$$

where, in the Mach-Helm-Ostwald terminology, the  $x_j$  are the "extensive variables" ( $S$ ,  $V$ ,  $n_i$ , etc.),

additive if the system is divided into parts. Similarly, the  $X_j$  are the corresponding "intensive variables" given the appropriate sign ( $T, -P, \mu_i$ , etc.). The sum  $j$  extends over all couples of variables that determine the state of the system under consideration. We do not wish to enter a discussion on the question how "logical" the names "intensive" and "extensive" variables are. We simply consider these notions defined in terms of equation (27) (20). Several sets of alternative names such as "generalized coordinates" (the  $x_j$ ) and their "conjugate forces" (the  $X_j$ ) have been suggested. In terms of these quantities the following equations are obtained:

$$(\partial X_j / \partial x_j)_{X_k, \text{ etc.}} < (\partial X_j / \partial x_j)_{x_k, \text{ etc.}} \quad (28a)$$

$$(\partial x_j / \partial X_j)_{X_k, \text{ etc.}} > (\partial x_j / \partial X_j)_{x_k, \text{ etc.}} \quad (28b)$$

The  $(X_j, x_j)$  couple may be called the "action" variables the  $(X_k, x_k)$  couple the "reaction" variables, and the remaining couples the "other" variables (11). The word "etc." appearing in each partial differential is meant to indicate that for the validity of equations (28a) and (28b) it is irrelevant which of the "other" intensive or extensive variables are kept constant. Note also that a possible minus sign appearing with an  $X$  in (27) does not affect equations (28). It is easily seen, by comparison of the expressions (12) and (27) for  $dE$ , that the results (20) and (26) are special cases of the equations (28a) and (28b), respectively. We can now also easily write down a more explicit equation, which embodies the result (1):

$$(\partial S / \partial T)_{A, \text{ etc.}} > (\partial S / \partial T)_{\xi, \text{ etc.}} \quad (29)$$

In many applications to chemical equilibria the reaction variables are the affinity,  $A$ , and the degree of advancement,  $\xi$ . In these cases equations (28) take on a slightly less abstract form, which may be put into words as follows:

*The change of an intensive variable caused by changing the corresponding extensive variable is smaller if chemical equilibrium is maintained than if no reaction could take place in the system.—(IIa)*

*The change of an extensive variable caused by changing the corresponding intensive variable is larger if chemical equilibrium is maintained than if no reaction could take place in the system.—(IIb)*

Again the Ehrenfest dichotomy is apparent. We should remember, however, that all these dual formulations are simply two aspects of what is essentially the same mathematical expression.

#### ADDING A COMPONENT TO A REACTION MIXTURE; AMMONIA FORMATION

When we add a component (21) we no longer are dealing with closed systems. We assume for simplicity that we only add one of the reacting substances, which we shall denote by  $j$ . Generalizations are obvious. We may now write:

$$dn_j = d_e n_j + d_i n_j \quad (30)$$

where  $d_e n_j$  refers to external changes in  $n_j$ , caused by adding some  $j$  from outside, and  $d_i n_j$  to internal changes in  $n_j$ , caused by a chemical reaction within the system. For such an open system the equation for the internal energy change takes the form:

$$dE = TdS - PdV - Ad\xi + \mu_j d_e n_j \quad (31)$$

where the term  $\mu_j d_e n_j$  is contained in  $Ad\xi$ . In analyz-

ing the effect of the addition of some  $j$ , we must clearly specify the conditions. We shall choose constant temperature,  $T$ , and constant total pressure,  $P$ . Now, by (28a):

$$(\partial \mu_j / \partial_e n_j)_{P, T, A} \cdot \delta_e n_j < (\partial \mu_j / \partial_e n_j)_{P, T, \xi} \cdot \delta_e n_j \quad (32)$$

This implies that the "primary" increase in  $\mu_j$  caused by the external addition is opposed by the equilibrium shift. In other words: *The induced chemical reaction has to lower  $\mu_j$ .*

This is the starting point of our subsequent analysis. At this point, the most important observation to make about this result, (32), is that it does not as yet allow us to draw any conclusion as to the direction of the equilibrium shift or, in our terminology, as to the sign of  $\delta\xi$ . The simplest example, that of a reaction between ideal gases, shows all the essential features for our purpose. We therefore restrict ourselves to this case. We then have:

$$\mu_j = \mu_j^\circ + RT \ln p_j \quad (33)$$

where  $\mu_j^\circ$  is a function of  $T$  only and  $p_j$  is the partial pressure of component  $j$ . By (33), if the equilibrium shift has to cause a decrease in  $\mu_j$ ,  $p_j$  has to decrease. By definition:

$$p_j = (n_j / \sum n) P \quad (34)$$

so that, at constant  $P$ :

$$(\partial p_j / \partial \xi)_P = [P / (\sum n)^2] [\sum n (\partial n_j / \partial \xi)_P - n_j (\partial \sum n / \partial \xi)_P] \quad (35)$$

But by (10):

$$\partial n_j / \partial \xi = \nu_j$$

and:

$$\partial \sum n / \partial \xi = \sum \nu$$

which yields in (35):

$$(\partial p_j / \partial \xi)_P = [P / (\sum n)^2] (\nu_j (\sum n) - n_j (\sum \nu)) \quad (36)$$

In this derivation no reference is made as yet to any specific (ideal) gas reaction. The result shows that the all important sign of  $(\partial p_j / \partial \xi)$  is dependent on the relative magnitude of  $\nu_j (\sum n)$  and  $n_j (\sum \nu)$ . Either of these two terms may exceed the other.

Let us now consider specifically the reaction:



and add some  $\text{N}_2$  to the equilibrium mixture at constant  $P$ . With the convention we adopted for the use of equation (9), we have  $\nu_j = -1$  and  $\sum \nu = -2$ . Thus equation (36) becomes:

$$(\partial p_{\text{N}_2} / \partial \xi)_P = [P / (\sum n)^2] [2n_{\text{N}_2} - \sum n] \quad (37)$$

In other words, if  $2n_{\text{N}_2} > \sum n$  (if the original mixture contains more than 50 mole %  $\text{N}_2$ ):

$$(\partial p_{\text{N}_2} / \partial \xi)_P > 0 \quad (38)$$

But, as we saw above, addition of  $\text{N}_2$  requires a decrease in  $p_{\text{N}_2}$ , hence by (38)  $\xi$  must also decrease, which in turn means that the equilibrium has to be shifted to the left: Adding  $\text{N}_2$  under these circumstances, which are by no means unrealistic, causes decomposition of some  $\text{NH}_3$  under the formation of even more  $\text{N}_2$ . Obviously the crux of the matter is that under these circumstances an equilibrium shift to the right would

cause such a large volume contraction, that  $p_{N_2}$  would have increased notwithstanding a decrease in  $n_{N_2}$ .

### VAN'T HOFF'S "PRINCIPLE OF MOBILE EQUILIBRIUM"

The well-known equations for ideal gases:

$$(\partial \ln K_p / \partial T)_P = \Delta H^\circ / RT^2 \quad (39)$$

and:

$$(\partial \ln K_c / \partial T)_V = \Delta E^\circ / RT^2 \quad (40)$$

are usually referred to as the van't Hoff "reaction isobar" and "reaction isochor," respectively. Indeed, in 1884 (3) van't Hoff was the first one to derive a relation essentially equivalent to (40) and it was upon this equation that he based his "principle of mobile equilibrium":

*An increase in temperature causes an equilibrium to be displaced in the direction of heat absorption (causes an endothermic reaction to take place)—(IIIi).*

In 1898 this rule was supplemented by the following (22):

*An increase in pressure (at constant temperature) causes an equilibrium to be displaced in the direction of volume contraction—(IIIii).*

The latter statement has been related to the equation:

$$(\partial \ln K_N / \partial P)_T = -\Delta V / RT \quad (41)$$

where  $K_N$  is the equilibrium constant in terms of mole fractions ( $K_p$  and  $K_c$  are independent of pressure), although we cannot find such a formula in van't Hoff's writings. It is true that van't Hoff claims a validity for his rules which reaches far beyond the immediate range of applicability of equations (39), (40), (41), but he never attempts to generalize in the manner of Le Chatelier and Braun. Even in 1898, he never referred to their work at all.

A simple analysis reveals that (IIIi) and (IIIii) are implied in the second [(IIb)] half of the general principle as formulated above. Thus, the principle of mobile equilibrium immediately explains the fundamental result (1), and equation (39) offers a powerful quantitative correlation. But there is no analogous counterpart to the other [(IIa)] half of the general formulation. Ipso facto the van't Hoff rules cannot account for inequalities such as (2).

This brief survey shows that it is at least inelegant to refer to the original rule (I) as the "Principle of Le Chatelier and van't Hoff," as is sometimes done explicitly and more often implicitly. On the one hand, Le Chatelier should not share in the credit for the formulation of the principle of mobile equilibrium. On the other hand, the more ambitious generalizations should not be attributed to van't Hoff.

### CONCLUSIONS

The original Le Chatelier-Braun principle in the form (I) has been called a "Principle of Moderation," a "Principle of Action and Reaction" (Nernst), a "Principle of ability of adaptation" (Chwolson) and a "Principle to preserve a status as much as possible" (Weinstein). Undoubtedly one of the main reasons for its popularity has been the possibility of such almost metaphysical interpretations. But as we have seen,

the actual situation does not justify any of these. To quote Max Planck (12):

The idea that nature has a certain interest to preserve an equilibrium state at all cost is wrong. Nature is essentially indifferent; in certain cases it reacts in one sense, but in other cases in the opposite sense.

The correct formulation (II) has lost all metaphysical flavor, and, with it, most popular appeal. It can only be properly understood in terms of some thorough thermodynamic treatment, which should find a place in most of our physical chemistry courses, certainly in the more advanced ones.

A review of the status of the Le Chatelier-Braun principle in general chemistry courses is long overdue. Its apparent usefulness may be ascribed to a combination of two factors:

A specific, otherwise entirely arbitrary, interpretation of a vague formulation such as (I), and

A careful restriction of the examples to those cases resorting under the second [(IIb)] half of the correct rule.

The latter restriction suggests that many of the successful applications are really direct consequences of van't Hoff's more restricted principle of mobile equilibrium. Any consistent interpretation of (I) has to lead to contradictions if we no longer limit our examples to those of one category. In fact it is of both didactic and historic interest to relate that Ehrenfest was first induced to examine critically the principle when one of his students pointed out to him that applications in some cases led to incorrect predictions (6).

Formulations such as (II) and alternative correct formulations known to the author (see references (10–16)) are unsuitable for elementary courses. What action can we take? To us, at this stage, the most promising procedure seems to be to replace the Le Chatelier-Braun principle by a small number of rules each of which has a limited range of applicability and is less ambitious (such as the ones given by van't Hoff), but which, on the other hand, allows for one and only one interpretation and may ultimately be justified on thermodynamic grounds.

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