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Thermodynamics and the Le Chatelier's Principle

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ABSTRACT. The limited character of the Le Chatelier's principle and its ambiguous and vague formulation have all been sufficiently expounded on. Nevertheless, on a teaching context, it is still used as an infallible principle without showing its limitations which can lead to very important misconceptions. Five cases, in which the Le Chatelier's principle can be misapplied, are studied herein while supplying an alternative thermodynamic approach. Basically, the following cases are given for systems in chemical equilibrium. a) Adding or eliminating one of the substances which are involved in the equilibrium mixture, at constant temperature and pressure. b) An inert gas is added at constant volume and temperature. c) Adding an inert gas at constant temperature and pressure. d) Changing the temperature at constant volume. e) Changing the temperature to saturated solutions. Finally, the proposal put forth is that in a teaching context, the Le Chatelier's rule be replaced by an in-depth analysis based on the laws of thermodynamics.

RESUMEN. El carácter limitado del principio de Le Chatelier, así como su formulación vaga y ambigua, han sido suficientemente tratados. Sin embargo, en un contexto puramente didáctico, el principio de Le Chatelier sigue usándose como un principio infalible, sin hacer referencia a sus limitaciones, lo cual puede originar importantes errores conceptuales. Se estudian cinco casos en los que el principio puede ser incorrectamente aplicado, proporcionándose al mismo tiempo un tratamiento termodinámico alternativo. Se estudian los siguientes casos para sistemas en equilibrio químico. a) Adición o eliminación, a presión y temperatura constantes, de una de las sustancias que participan en la mezcla de equilibrio. b) Adición de un gas inerte a volumen y temperatura constantes. c) Adición de un gas inerte a presión y temperatura constantes. d) Variación de la temperatura a volumen constante. e) Variación de la temperatura en disoluciones saturadas. Finalmente, se propone que en un contexto didáctico, la regla de Le Chatelier sea reemplazada por un profundo análisis basado en las leyes de la termodinámica.

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1. INTRODUCTION

It has always been advantageous, both from a practical and from a teaching point of view, to have qualitative sweeping rules which predict the development of chemical systems whenever the variables defining them are altered. In the discussion of the evolution of perturbed chemical equilibria, a *principle of moderation*, first formulated in 1884 by H.L. Le Chatelier [1], has played a very important role.

It has been sufficiently expounded on in papers [2–25] and in advanced textbooks [26–31] the limited character of the Le Chatelier's principle and its ambiguous and vague formulation. In spite of the broad attack on the Le Chatelier's principle launched by some of the above authors and the eloquence of their works, their concern has been largely ignored by authors of general chemistry textbooks. A recent paper [32] reported on the extensive use of the le Chatelier's principle in high-school and first-year university general textbooks in which its formulation mostly follows the 1888 and 1908 Le Chatelier's statements [33,34], which is usually presented, by the positivistic claim, as an infallible principle without showing its limitations. Moreover, Quílez and Sanjosé [35] ascertained that chemical equilibrium exams, as a rule, set forth problems whose statements seems to leave out, for the most part, the variables which remain constant when the equilibrium is disturbed. The implication is that teachers want their students to apply the Le Chatelier's principle as an infallible rule to solve the problem. Hence, this teaching methodology, in which rules are automatically applied without defining either the field of application or the limitations of the principles and in which the hypothetical-deductive thought processes are not fostered, is liable to produce low levels of meaningful learning in that simple association rules are employed to solve repeated drills, eliciting "correct answers" depending on how well acquainted (contiguity and frequency) the student is with the task at hand, wherein his/her ability to give explanations and reasons might be shown to be poor. As a result, some difficulties and misconceptions about the effect of changing conditions on a chemical equilibrium mixture have been reported [32,35]. In most of first-year university students as well as teachers, the intent of application of the Le Chatelier's principle leads to the following incorrect rule: "If a reactive is added to a chemical equilibrium mixture, the equilibrium will always shift to produce a greater amount of products (and vice-versa). Thus, the effect of adding an inert chemical will not change the equilibrium mixture".

This work will peruse the various situations in which the intent of application of the Le Chatelier's principle, as it is usually formulated in textbooks, may lead to the exact reverse of the truth. Additionally, in each case a thermodynamic analysis will be carried out to establish concrete answers regarding the evolution of a chemical equilibrium mixture which has been disturbed. Finally, depending on the analysis proffered, proper arguments will be presented as to the viability of substituting the Le Chatelier's principle in teaching chemical equilibrium.

2. THERMODYNAMICS AND THE LE CHATELIER'S PRINCIPLE

Le Chatelier's principle is qualitative and cannot be used to predict the effect on an equilibrium of changing simultaneously factors that have different directional effects on the equilibrium shift. This section will highlight different cases attempting to apply it under an inappropriate set of conditions while at the same time presenting an alternative thermodynamic approach. To this end, five different situations will be analyzed underscoring the applicability of the thermodynamic approach as opposed to the various endeavors to apply the Le Chatelier's principle to find the answer to each five cases.

2.1. Adding or eliminating one of the substances of the equilibrium mixture at constant pressure and temperature

For instance, we have a mixture of ideal gases in equilibrium as expressed by the following equation:

$$aA(\mathrm{g}) + bB(\mathrm{g}) \Leftrightarrow rR(\mathrm{g}) + sS(\mathrm{g}). \tag{1}$$

If one of the products, $R(\mathrm{g})$, is added to the equilibrium mixture and an attempt is made to predict which side the equilibrium will shift to, we could superficially base our answer on the Le Chatelier's principle and predict a shift to the left side to form a larger quantity of reactives. But, we must keep in mind that the addition has been made under constant pressure, causing an increase in partial pressure of $R(\mathrm{g})$, while that of $S(\mathrm{g})$ decreases (and also those of reactives decrease). Therefore, two variations are produced simultaneously and, according to the Le Chatelier's principle, each leading to opposite shifts; that is, there is no way we can predict the reaction shift. The same conclusion can be arrived at if we reason based on the variance in the concentration of each chemical, keeping in mind that adding the gas will cause the volume of the reactor to increase.

Adding $R(\mathrm{g})$ at constant pressure and temperature will provide an increase in its concentration. The system will evolve in such a way that this increase will be diminished. Nonetheless, its mass variation need not to follow the same tendency. A decrease in $R(\mathrm{g})$ concentration could be brought by increasing its mass as long as the reactor volume increases sufficiently. If a certain amount of $R(\mathrm{g})$ is to be eliminated, at constant temperature and pressure, arguments similar to the above could be propounded, stumbling again when it comes to the application of the principle.

Next we shall see how thermodynamics provides an answer to the situation put forth. As a starting point, the following equation can be presented based on the mixture of ideal gases as in (1):

$$\Delta G = RT \ln \frac{Q_p}{K_p^0}, \tag{2}$$

yielding the reaction Gibbs function (ΔG) based on the reaction quotient, Q_p, defined as

$$Q_p = \prod_i \left(\frac{P_i}{P^0}\right)^{\nu_i} = \prod_i \frac{n_i^{\nu_i}}{n^{\Delta\nu}} \left(\frac{P}{P^0}\right)^{\Delta\nu}, \qquad (P^0 = 1 \text{ bar}), \tag{3}$$

and of the equilibrium constant, K_p^0, defined as

$$K_p^0 = \prod_i \left(\frac{P_{i,\,\mathrm{eq}}}{P^0}\right)^{\nu_i}. \tag{4}$$

When the mixture is disturbed by means of adding (or eliminating) one of the components in the equilibrium mixture (R, for instance) while P and T remain constant, the spontaneous evolution of the mixture is such that $d(\Delta G)\,d\epsilon < 0$, where

$$d(\Delta G) = d\left(RT\ln\frac{Q_p}{K_p^0}\right) = RT\,d\ln Q_p, \tag{5}$$

and consequently, according to the sign of

$$\left(\frac{\partial \ln Q_p}{\partial n_R}\right)_{P,T,n_{i\neq R}}, \tag{6}$$

the equilibrium mixture will shift to the right ($d\epsilon > 0$) or to the left ($d\epsilon < 0$). Actually, if we add R(g) and the sign of (6) is positive, the mixture will evolve toward the left, while if it is negative, more products will be formed.

If such derivative is carried out from (3), we finally would have

$$\left(\frac{\partial \ln Q_p}{\partial n_R}\right)_{P,T,n_{i\neq R}} = \frac{r - \Delta\nu\, X_R}{n_R}, \tag{7}$$

where X_R is the molar fraction of R ($n_R/\sum n_i$).

Equation (7) tells us that the mixture will produce a greater amount of reactives if X_R is less than the $r/\Delta\nu$ factor; otherwise, a greater amount of products would be produced.

We may apply these theoretical considerations to different equilibria which we will view as examples. Thus, we can consider first the thermal decomposition of the ammonia carbamate:

$$\mathrm{NH_2CO_2NH_4(s)} \rightleftharpoons \mathrm{CO_2(g)} + 2\,\mathrm{NH_3(g)}$$

wherein, once the equilibrium has been established, carbon dioxide is added while P and T remain constant building a larger amount of gases if $X(\mathrm{CO_2}) > 1/3$. If we were to condition the ammonia to this effect, we could obtain $X(\mathrm{NH_3}) > 2/3$.

Secondly, we will mention as examples two processes of great industrial importance: the ammonia and the methanol syntheses. In the ammonia synthesis according to the Haber-Bosch process,

$$\mathrm{N_2(g)} + 3\,\mathrm{H_2(g)} \rightleftharpoons 2\,\mathrm{NH_3(g)},$$

one may think that adding cheaper synthesis gas would bring about an increase in the rate of hydrogen conversion and that more ammonia would be produced [23]. But, adding nitrogen to the equilibrium mixture will cause the decomposition of a large amount of ammonia if $X(\mathrm{N_2}) > 1/2$. In the industrial synthesis of methanol, according to the following equation:

$$\mathrm{CO(g)} + 2\,\mathrm{H_2(g)} \rightleftharpoons \mathrm{CH_3OH(g)},$$

adding carbon monoxide to the equilibrium mixture will cause decomposition of methanol if $X(\mathrm{CO}) > 1/2$.

2.2. Adding an inert gas to a gaseous mixture in chemical equilibrium, at constant volume and temperature

The following explanation may be given in trying to apply the Le Chatelier's principle to explain what happens if an inert gas is added to a chemical equilibrium mixture at constant volume an temperature [15]: "Addition of the inert gas at constant volume and temperature will increase the total pressure. The Le Chatelier's principle suggests that the system will adjust itself in such a way that this increase in pressure will be minimized somewhat. This can be achieved by the less number of molecules reaction proceeding to a greater extent than previously".

If we take a thermodynamic approach analogous to the one carried out in the previous section, we should then analyze how Q_p varies with regard to the number of moles of the inert gas (G):

$$\left(\frac{\partial \ln Q_p}{\partial n_G}\right)_{V,T,n_{i\neq G}} \tag{8}$$

Starting from Q_p,

$$Q_p = \prod_i n_i^{\nu_i}\left(\frac{P}{P^0 n}\right)^{\Delta\nu} = \prod_i n_i^{\nu_i}\left(\frac{RT}{P^0 V}\right)^{\Delta\nu}, \tag{9}$$

where $n = n_i + n_G$, we may see that if T and V remain constant, Q_p does not change due to the addition of G and therefore the derivative (8) is naught and $d(\Delta G) = 0$; that is to say, the equilibrium has not been disturbed.

2.3. Adding an inert gas to a gaseous equilibrium mixture at constant pressure and temperature

An inert substance added under these conditions disturbs the equilibrium by reducing the concentrations of all reactants and products. As pointed out previously, Le Chatelier's principle cannot be used to predict the effect on an equilibrium of changing simultaneously factors that have different directional effects on the equilibrium shift. This addition means an increase in the volume of the isothermal and isobar reactor, to which the Le Chatelier's principle has no satisfactory answer, but the laws of thermodynamics do provide one. Let us take a look.

The disturbance in the volume causes a variation of Q_p, which after adding the inert gas, G, becomes

$$Q_p = \prod_i n_i^{\nu_i}\left[\frac{P}{P^0(\sum n_i + n_G)}\right]^{\Delta\nu}, \tag{10}$$

from which can be obtained the following equation:

$$\left(\frac{\partial \ln Q_p}{\partial n_G}\right)_{P,T,n_{i\neq G}} = -\frac{\Delta\nu}{n}. \tag{11}$$

As is easily discernible, the sign of the derivative and consequently the direction of the shift in the equilibrium mixture will depend on the sign of $\Delta\nu$. Thus, if $\Delta\nu$ is negative, then $d(\Delta G) > 0$ and $d\epsilon < 0$, that is, the addition of an inert gas will cause a shift in the equilibrium mixture to the left. The opposite effect causes the addition of the inert gas if $\Delta\nu > 0$.

2.4. Changing the temperature at constant volume

Let us continue with the same reaction of ideal gases (1) and let us assume that there is a constant volume, that is exothermal ($\Delta H^0 < 0$) and that $\Delta\nu < 0$. If the reactor is heated or cooled toward which end will the equilibrium mixture shift?

Starting with an increase of T at constant V, the effect is a simultaneous increase of P. According to the Le Chatelier's principle, both disturbances will produce opposite effects and hence the inability to foretell the direction of the mixture shift. Once again, let us see how thermodynamics offers and exact answer to this case.

The change in ΔG since P and T were adjusted, while the composition of the mixture remains the same, is expressed thus:

$$d(\Delta G) = \left(\frac{\partial\,\Delta G}{\partial T}\right)_{P,\epsilon} dT + \left(\frac{\partial\,\Delta G}{\partial P}\right)_{T,\epsilon} dP, \tag{12}$$

where

$$\left(\frac{\partial\,\Delta G}{\partial T}\right)_{P,\epsilon} = -\Delta S^0, \tag{13}$$

$$\left(\frac{\partial\,\Delta G}{\partial P}\right)_{V,\epsilon} \doteq \Delta V^0, \tag{14}$$

and if the change in T comes about while the mixture is in equilibrium and we suppose an ideal behaviour of the gases, we can write

$$\Delta S^0 = \frac{\Delta H^0}{T} = \frac{\Delta U^0 + \Delta\nu\, RT}{T} \tag{15}$$

and

$$dP = \frac{\Delta\nu\, RT}{\Delta V^0}. \tag{16}$$

While making the necessary replacements of (13), (14), (15) and (16) in (12), the following can be deduced:

$$d(\Delta G) = -\frac{\Delta U^0}{T}\, dT, \tag{17}$$

wherein, when we take into account the criterion of spontaneous evolution $d(\Delta G)\, d\epsilon < 0$:

$$\frac{dT\, \Delta U^0\, d\epsilon}{T} > 0 \tag{18}$$

Two facts must be highlighted in this last equation. Firstly, that thermodynamics indicates that the effects of simultaneous adjustment of the intensive variables P and T can be predicted by means of the variation of just one of them. (T, for example). Second, the direction of the shift in the equilibrium mixture will depend on the sign of ΔU^0. This should make us reflect on the indiscriminate use of ΔH^0. So for instance, the reaction taking place at constant volume,

$$2\,CO_2(g) + 4\,H_2(g) \rightleftharpoons CH_3OH(l) + CO(g) + H_2O(l),$$

in certain specific conditions of P and T (1 atm, 300 K) has a very small enthalpy of reaction of negative sign ($\Delta H = -8.4$ kJ) [36]. This way if T is increased, the sign of ΔU^0 could be different from that of ΔH^0. This could mean that a specific increase of T would cause the mixture to shift in the opposite direction foreseen according to ΔH^0.

2.5. *Temperature dependence of the solubility of salts*

The dependence of the solubility of solids in water with regard to the temperature is frequently analyzed by means of the Le Chatelier's principle. It predicts that solubility will increase with temperature if the dissolution is endothermical ($\Delta H > 0$) and will decrease if the dissolution is exothermical ($\Delta H < 0$) (Of course, you can only reason this way sensu stricto if the dissolution is saturated, as this is the only instance when the mixture would be in true chemical equilibrium). Even though in most cases the prediction comes true, the validity of the principle has been questioned [37–39]. NaOH and $NaC_2H_3O_2$ are examples of substances which dissolve exothermically and whose solubility increases with the temperature.

Let us carry out a thermodynamic analysis of the equilibrium mixture between the particles of a substance B in the solid matter and in the saturated water dissolution:

$$B(s) \rightleftharpoons B(sat). \tag{19}$$

Under such conditions the chemical potencial of B ought to be identical in both phases:

$$\mu_B(s) = \mu_B(sat) \tag{20}$$

Any infinitesimal equilibrium change caused by the variation of T will lead to

$$d\mu_B(s) = d\mu_B(sat). \tag{21}$$

Just as the chemical potential depends on P, T and c_B (molality or molar fraction of B), the differential at constant pressure is expressed as

$$d\mu_B = \left(\frac{\partial\mu_B}{\partial T}\right)_{P,c_B} dT + \left(\frac{\partial\mu_B}{\partial c_B}\right) dc_B, \tag{22}$$

and since

$$\left(\frac{\partial\mu_B}{\partial T}\right)_{P,c_B} = -\bar{S}_B \tag{23}$$

we would have to

$$d\mu_B(s) = -\bar{S}_B(s)\,dT, \tag{24}$$

$$d\mu_B(sat) = -\bar{S}_B(sat)\,dT + \left(\frac{\partial\mu_B}{\partial c_B}\right)_{P,T} dc_B, \tag{25}$$

where $\bar{S}_B(sat)$ is the partial molar entropy of B in the saturated dissolution.

On the other hand, in the equilibrium $\Delta\bar{G}_B = 0$ which would then be

$$\bar{S}_B(sat) - \bar{S}_B(s) = \frac{\bar{H}_B(sat) - \bar{H}_B(s)}{T} = \frac{\Delta\bar{H}_B(sat)}{T}, \tag{26}$$

where $\Delta\bar{H}_B(sat)$ is the so-called differential heat of the dissolution of B in the saturated dissolution. From this we may deduce that (21) could be formulated thus:

$$\frac{\Delta\bar{H}_B(sat)}{T}\,dT = \left(\frac{\partial\mu_B}{\partial c_B}\right)_{P,T} dc_B; \tag{27}$$

from this we could obtain the variation of the concentration of B (or its solubility) with the temperature:

$$\frac{dc_B}{dT} = \frac{\Delta\bar{H}_B(sat)}{T\left(\frac{\partial\mu_B}{\partial c_B}\right)_{P,T}}, \tag{28}$$

which shows that the only factor affecting the said variation is the sign of $\Delta\bar{H}_B(sat)$, since the denominator is always positive.

This result coincides with other similar theoretical analyses [40,41] and reveals that for the solubility prediction of a solid with regard to temperature, the sign of the dissolution heat (ΔH) is of no consequence, rather the sign of the heat differential of solids in saturation, $\Delta \bar{H}(\mathrm{sat})$, that is the sign belonging to the derivative

$$\left(\frac{\partial \Delta H}{\partial n_{\mathrm{B}}}\right)_{P,T,n_{\mathrm{A}}} \qquad (\mathrm{A} = \mathrm{solvent}) \tag{29}$$

in the saturated dissolution of B.

This explains why NaOH and $NaC_2H_3O_2$ dissolve more easily at higher temperatures despite their exothermical dissolution: their $\Delta \bar{H}_{\mathrm{B}}(\mathrm{sat})$ is greater than zero.

Differential heats of solution at saturation must be used when predicting the effect of temperature on solubility. If this is done, Le Chatelier's principle makes no incorrect predictions.

3. CONSEQUENCES

We have analyzed the difficulties that the Le Chatelier's principle (more appropriately termed, the Le Chatelier's rule) encounters when applied according to the statements presented by the author himself which are used in teaching the evolution of a perturbed chemical equilibrium mixture. Nonetheless, we point out that this rule has been reformulated which has given a wider validity [13,14,18,27,29,30] but, at the same time, it has been made more complicated, so much so that it has lost its usefulness at elementary chemistry courses. Other authors [31,42–47] have restricted it to variations of T to P constant as well as of P to T constant. Therefore, it is suggested that, as teachers, these are the conditions we should preferably use the Le Chatelier's principle.

For our part, we propose that in teaching chemical equilibrium at university, the Le Chatelier's rule be replaced by an in-depth analysis of the thermodynamic laws. Basically, this analysis can be summarized in the following sections:

1) To predict the evolution of disturbed chemical equilibrium mixtures:

a) Whenever the disturbance of the mixture is isothermal, and therefore the equilibrium constant, K^0, does not vary, utilizing the reaction quotient, Q, by means of the equation

$$\Delta G = RT \ln \frac{Q}{K^0}. \tag{30}$$

If $Q = K^0 (\Delta G = 0)$ the system is at equilibrium.
If $Q > K^0 (\Delta G > 0)$ the spontaneous direction of reaction is products → reactives.
If $Q < K^0 (\Delta G < 0)$ the spontaneous reaction is reactives → products.

b) Using isobar and isocore van't Hoff's equations whenever the temperature of the mixture is changed:

$$\frac{d \ln K_p^0}{dT} = \frac{\Delta H^0}{RT^2} \quad (P = \text{constant}), \tag{31}$$

$$\frac{d \ln K_c^0}{dT} = \frac{\Delta U^0}{RT^2} \quad (V = \text{constant}). \tag{32}$$

If $\Delta H^0 > 0$ or $\Delta U^0 > 0$:

- $dT > 0$, then $dK^0 > 0$: shift reactives → products
- $dT < 0$, then $dK^0 < 0$: shift products → reactives

If $\Delta H^0 < 0$ or $\Delta U^0 < 0$:

- $dT > 0$, then $dK^0 < 0$: shift products → reactives
- $dT < 0$, then $dK^0 > 0$: shift reactives → products

2) When regarding the study of solubility of solids with temperature, the introduction of the concept of differential heat of the dissolution in the saturation, $\Delta \bar{H}_{\mathrm{B}}(\text{sat})$, and the explanation of the variance in solubility with the temperature depends on the sign of said differential heat:

If $\Delta \bar{H}_{\mathrm{B}}(\text{sat}) > 0$ and $dT > 0$, then $dc_{\mathrm{B}} > 0$;
and $dT < 0$, then $dc_{\mathrm{B}} < 0$.

If $\Delta \bar{H}_{\mathrm{B}}(\text{sat}) < 0$ and $dT > 0$, then $dc_{\mathrm{B}} < 0$;
and $dT < 0$, then $dc_{\mathrm{B}} > 0$.

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