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CHEMICAL REACTIONS DO NOT ALWAYS MODERATE CHANGES IN CONCENTRATION OF AN ACTIVE COMPONENT

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Abstract. It is shown in this paper that the use of Le Chatelier's principle as a Principle of Moderation fails. It is discussed moderation of mole fractions and moderation of molar concentration (molarity) in a reaction of ideal gases. An analysis carried out on thermodynamic grounds allows us to conclude that this system moderates the increment of molar concentration (molarity) of an active component, but this same system does not moderate the increment of mole fraction of an active component at constant T and V.

Keywords: chemical equilibrium, changes in concentration, Le Chatelier's principle, moderation of molar concentration, moderation of mole fractions.

Introduction

A deep understanding of how various factors affect a chemical system at equilibrium is an important aspect of general and physical chemistry courses. Most high school and college chemistry textbooks rely on Le Chatelier's principle to predict the direction of shift in a chemical equilibrium when it is subjected to a perturbation. Considerable attention has been dedicated to the discussion and applications of the Le Chatelier's principle (Canagaratna, 2003; Corti & Franses, 2003). Prigogine & Defay (1954) call it the Moderation Theorem and they suggest that the principle suffers from a number of important exceptions and that systems involving irreversible changes may also under certain circumstances obey it. According to Glansdorff & Prigogine (1971) the Le Chatelier's principle implies moderation with respect to the change of an intensive variable.

In this article we make a thermodynamic analysis of the evolution of a system of ideal gases in chemical equilibrium that shows why this system may not moderate with respect to the increment of the mole fraction (intensive variable) at constant temperature, T, and volume, V. Nevertheless, this same system moderates the increment of the molar concentration (molarity, intensive variable) both at constant temperature, T, and pressure, P, and at constant T and V.

Perturbation of a chemical equilibrium and affinity

For a system of various constituents in chemical equilibrium, we shall write the chemical equation as

$$\sum_i \nu_i B_i(p_i) = 0 \tag{1}$$

where ν_i is the stoichiometric number of species *i* (by convention, positive for products and negative for reactants), B_i is the chemical formula and p_i is the physical state of i. The total differentials of Gibbs Free Energy *G* and the Helmholtz Free Energy *F* take the form

$$dG = -SdT + VdP - \mathrm{A}\, d\xi \tag{2}$$

$$dF = -SdT - PdV - \mathrm{A}\, d\xi \tag{3}$$

where the ξ is the extent of reaction and the *A* is the affinity of the reaction (Modell & Reid, 1974). The extent of reaction can be written in terms of the quantities (in moles) of species n_i and the stoichiometric coefficients ν_i of the corresponding substances *i*, in the form

$$d\xi = \frac{dn_i}{\nu_i} \tag{4}$$

The affinity of the reaction, which is the negative of the reaction Gibbs energy, $\Delta_r G$, is defined as

$$\mathrm{A} = -\sum_i \nu_i \mu_i = -\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = -\left(\frac{\partial F}{\partial \xi}\right)_{T,V} \tag{5}$$

where μ_i is the chemical potential of species *i.* The affinity is a function of variables defining the state of the system (*T, P* and ξ, for instance) and has always the same value for a given state, regardless of the nature of the transformation experienced by the system (Martinez, 2007).

Thus, from Eq. (2) and Eq. (3), the criterion for chemical equilibrium, regardless of what sets of variables (*T, P*) or (*T, V*) are kept constant, may be written as $A = 0$. If a system is not in equilibrium, any reaction must satisfy the condition that

$$\mathrm{A}\, d\xi > 0 \tag{6}$$

Let us consider a system defined by the independent variables *T, P* and ξ which is in a state 1 of chemical equilibrium, then

$$A_1(T, P, \xi) = 0 \tag{7}$$

If the system is perturbed to a state 2 which differs only infinitesimally from the initial state and is defined by $T + dT$, $P + dP$ and $\xi + d\xi$, the affinity must then be

$$A_2 = A_1 + dA = dA = \left(\frac{\partial A}{\partial T}\right)_{P,\xi} dT + \left(\frac{\partial A}{\partial P}\right)_{T,\xi} dP + \left(\frac{\partial A}{\partial \xi}\right)_{T,P} d\xi \tag{8}$$

From the Eq. (6) the direction of spontaneous change in the reaction, proceeding from state 2 toward the final equilibrium state can be written

$$A_2\, d\xi > 0 \tag{9}$$

or

$$dA\, d\xi > 0 \tag{10}$$

i.e., if $dA > 0$, then reaction proceeds to the right, $d\xi > 0$. If $dA < 0$, then reaction proceeds to the left, $d\xi < 0$.

Finally, let us consider an equilibrium state 3 having been achieved by a perturbation as previously discussed. Both the state 3 and the initial state 1 are states of equilibrium, but differing from one another in the values of the variables T, P and ξ, therefore,

$$A_3(T', P', \xi') = 0 \tag{11}$$

and the variation of the affinity on passing from state 1 to state 3 must be zero, $dA = 0$.

Moderation of mole fractions

Alberty (1987) and Brénon-Audat et al. (1993) noted for the familiar equilibrium

$$N_2(g) + 3\,H_2(g) \leftrightarrows 2\,NH_3(g) \tag{12}$$

that when more nitrogen is added at constant T and P the equilibrium shifts in such a way as to reduce the mole fraction of nitrogen that would have resulted if the equilibrium had been frozen. But, what happens when nitrogen is added at constant T and V?. We shall demonstrate that the equilibrium may not moderate the mole fraction of nitrogen.

Let us consider an ideal gas reaction

$$a\,A\,(g) + b\,B\,(g) \leftrightarrows c\,C\,(g) \tag{13}$$

For this system, we have

$$\mathrm{A} = RT\left(\ln K^0 - \ln\frac{P_C^c}{P_A^a P_B^b}\right) = RT\left\{\ln K^0 - \ln\left[\frac{n_C^c}{n_A^a n_B^b}\left(\frac{RT}{V}\right)^{\Delta\nu}\right]\right\} \tag{14}$$

where K^0 is the thermodynamic equilibrium constant and $\Delta\nu$ is the difference in stoichiometric numbers of products and reactants: $\Delta\nu = c - a - b$ (Gerhartl, 1994).

We shall suppose that the system is perturbed by addition of a small amount $d_e n_A$ of the reactant *A (g)* with *T, V* and the moles of *B (sg)* and *C (g)* constant. We are now interested in the moderation of the mole fraction of the component *A (g)* of the reaction (13)

$$y_A = \frac{n_A}{n} = \frac{n_A}{n_A + n_B + n_C} \tag{15}$$

If no reaction occurs as a result of the addition of *A (g)*, then the variation of the mole fraction of *A (g)* may be written

$$\frac{dy'_A}{y_A} = \frac{dn_A}{n_A} - \frac{dn}{n} = \left(\frac{1}{n_A} - \frac{1}{n}\right)d_e n_A \tag{16}$$

However, if addition of *A (g)* leads to an equilibrium displacement, the change in the number of moles of *A (g)* is caused by internal changes in the chemical reaction $-ad\xi$ and the transfer of matter from surroundings $d_e n_A$. We thus have

$$dn_A = -ad\xi + d_e n_A \tag{17}$$

and the change in the total number of moles *n*

$$dn = \Delta\nu\, d\xi + d_e n_A \tag{18}$$

Hence, the variation of the mole fraction of *A (g)* in the presence of equilibrium displacement may be written

$$\frac{dy_A}{y_A} = \frac{dn_A}{n_A} - \frac{dn}{n} = -\left(\frac{a}{n_A} + \frac{\Delta\nu}{n}\right)d\xi + \left(\frac{1}{n_A} - \frac{1}{n}\right)d_e n_A \tag{19}$$

The difference in the variations of mole fractions of A(g), $dy_A - dy'_A$, must be negative for the equilibrium displacement to moderate with respect to the increment of the mole fraction of A (g). Then, from Eqs. (16) and (19)

$$\frac{dy_A}{y_A} - \frac{dy'_A}{y_A} = -\left(\frac{a}{n_A} + \frac{\Delta\nu}{n}\right)d\xi = -\left(\frac{a + y_A\Delta\nu}{n_A}\right)d\xi < 0 \tag{20}$$

On the other hand, the system will tend to return to a new equilibrium state, and the variation of the affinity on passing from one state to another must be zero dA = 0. For the addition of $d_e n_A$ moles of A (g) followed by reaction to extent $d\xi$, at constant T and V,

$$d\mathrm{A} = \left(\frac{\partial \mathrm{A}}{\partial n_A}\right)_{T,V,n_B,n_C} d_e n_A + \left(\frac{\partial \mathrm{A}}{\partial \xi}\right)_{T,V} d\xi = 0 \tag{21}$$

But, from Eq. (14) we deduce

$$\left(\frac{\partial \mathrm{A}}{\partial n_A}\right)_{T,V,n_B,n_C} = \frac{RTa}{n_A} \tag{22}$$

Substituting in (21), we now obtain

$$\frac{d\xi}{d_e n_A} = -\frac{RTa}{n_A A'} \tag{23}$$

where A' is $\left(\frac{\partial \mathrm{A}}{\partial \xi}\right)_{T,V}$ or $-\left(\frac{\partial^2 F}{\partial \xi^2}\right)_{T,V}$. If the equilibrium considered is stable, then $A' < 0$ (it is sufficient that the thermodynamic potential Helmholtz free energy F be a *minimum*, kept at constant volume and temperature, be in a state of stable equilibrium). This Eq. (23) allows us to calculate the effect upon the position of equilibrium of the introduction of a certain amount $d_e n_A$ of A (g). Since $a > 0$, $d\xi$ has the same sign of the $d_e n_A$. There is, therefore, moderation with respect to the quantity (in moles) of A (g) at T and V constant.

Putting Eq. (23) in Eq. (20), we then obtain

$$\frac{dy_A}{y_A} - \frac{dy'_A}{y_A} = \frac{(a + y_A\Delta\nu)RTa}{n_A^2 \mathrm{A}'} d_e n_A < 0 \tag{24}$$

Provided that $d_e n_A$ is positive moderation of the mole fraction will be exhibited only when

$$a + y_A \Delta \nu > 0 \tag{25}$$

We notice in particular that if Δν > *0* the inequality is always satisfied since the coefficient *a* is positive. However, if Δν < *0* we find that the condition for moderation becomes

$$y_A < -\frac{a}{\Delta \nu} \quad \text{or} \quad y_A < \frac{a}{|\Delta \nu|} \tag{26}$$

It is interesting to note that the system does not moderate with respect to the increment of the mole fraction of *A (g)* when

$$y_A \geq \frac{a}{|\Delta \nu|} \tag{27}$$

The case of the addition (or removal) of reactant *B (g)* or product *C (g)* can be treated in a similar manner. Thus, in the synthesis of ammonia (12) for nitrogen *a* = 1 and Δν = –2. Hence, provided that $y_{N_2} \geq \frac{1}{2}$, the addition of a small amount of nitrogen at constant *T* and *V* is followed by a further formation of ammonia. However, the final mole fraction of nitrogen is still greater than it was immediately following the addition. For this case, the system does not moderate with respect to the variation of mole fraction.

Moderation of molar concentration

We now consider the moderation of molar concentration of *A (g)* with $d_e n_A$ moles of *A(g)* added at constant *T* and *V*, for the same system (13). Remembering the definition of molar concentration, we can immediately write for *A (g)*

$$c_A = \frac{n_A}{V} \tag{28}$$

where *V* is the volume of the mixture of ideal gases (13) expressed in litres.

Since the volume is constant, the variation of the c_A may be written

$$\frac{dc_A}{c_A} = \frac{dn_A}{n_A} \tag{29}$$

and the discussion of the change in the number of moles of *A (g)* follows the same lines as above. Thus, in absence of equilibrium shift

$$\frac{dc_A'}{c_A} = \frac{d_e n_A}{n_A} \tag{30}$$

and in the case of equilibrium shift

$$\frac{dc_A}{c_A} = \frac{-ad\xi + d_e n_A}{n_A} \tag{31}$$

For moderation to occur, the difference in the variations of molar concentrations of *A (g)* must be negative. That is

$$\frac{dc_A}{c_A} - \frac{dc_A'}{c_A} = \frac{-ad\xi}{n_A} < 0 \tag{32}$$

Regarding Eq. (23) one obtains that $d\xi$ has the same sign of the $d_e n_A$ (positive). Then, the difference $dc_A - dc_A'$ is always negative. If, therefore, we perturb our system by addition of a small amount of *A (g)* at constant *T* and *V*, the reaction proceeds in a direction such that the increment of the molar concentration of *A (g)* is reduced. The case of the addition (or removal) of reactant *B (g)* or product *C (g)* can be treated in a similar manner.

If the system (13) were perturbed by the addition of *A (g)* at constant *T* and *P*, the variation of the c_A would also be reduced. We can easily prove this by using Eq. (28) and substituting state equation of ideal gases

$$c_A = \frac{n_A P}{nRT} = \frac{y_A P}{RT} \tag{33}$$

Since *T* and *P* are constant, the variation of c_A is the same as the variation of y_A. Hence, moderation of molar concentration with respect to the addition of *A (g)* at constant *T* and *P* is exhibited by the system. Analogous statements may be made for reactant *B (g)* or product *C (g)*.

Summary and discussion

Moderation of mole fractions and moderation of molar concentration in an open system of ideal gases $a\ A\ (g) + b\ B\ (g) \leftrightarrows c\ C\ (g)$ have been discussed. It has been shown that the system may not moderate the increment of the mole fraction of an active component at constant *T* and *V*. However, the system always moderates the increment of molar concentration (molarity) of an active component, regardless of what set of variables (*T, V*) or (*T, P*) are kept constant. As a surprise, the rules of moderation, expressed by Eqs. (24) and (32), seem never to have been derived before. In any event, they are absent from standard textbooks.

Some authors have attempted to restate the Le Chatelier's principle more accurately by a process of analysis and re-synthesis. However, these formulations are expressed in terms and based on arguments which are probably unsuitable for undergraduate presentation. According to Treptow (1980) a brief, yet unambiguous way of phrasing Le Chatelier's principle is *"A system at equilibrium resists attempts to change its temperature, pressure, or concentration of a reagent."* In the present paper we illustrate that this formulation is valid only with proper choice of the concentration scale. The concentration must be expressed in molar concentration. In this way, the principle can be satisfactorily applied to open systems to which substances have been added or removed. Nevertheless, the most promising procedure seems to be to replace the principle by teaching strategies based on a thermodynamic study which would consider the use of the chemical equilibrium law and the laws of van't Hoff (Quilez & Solaz-Portolés, 1995). On the other hand, the paper of Solaz-Portolés & Quílez (2001) tries to fill the gap resulting from the lack of a relevant advanced thermodynamic discussion on the variation of ξ in open systems, and to find the mathematical expressions of the variation of ξ with the infinitesimal variation in the mass of a chemical equilibrium mixture.

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