

EXCEPTIONS TO THE LE CHATELIER PRINCIPLE

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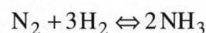
When studying chemical reactions within a single phase, chemical engineers require knowledge of the equilibrium constants. For a given temperature and pressure, equilibrium compositions may then be calculated for all relevant reactions. If the temperature, pressure, or composition of one of the components changes, however, the equilibrium position usually shifts. The direction of such shifts can be calculated by direct computation of the new equilibrium state.

Observations of the direction of shifts in the equilibrium position led to the formulation of a general statement referred to as the "Principle of Le Chatelier,"^[1] or sometimes as the "Principle of Le Chatelier and Braun."^[2] Le Chatelier's principle can be stated as follows:^[1]

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.

The above statement is useful in inferring, without direct calculation, the effects of changes in a system initially at equilibrium. Yet, still not widely known, particularly in the chemical engineering literature, is that Le Chatelier's principle is not universally valid, and exceptions are known to occur. (See, however, Sandler^[2] and Tester and Modell^[3] as examples of current chemical engineering textbooks that highlight the limitations of the above statements. Exceptions to Le Chatelier's principle appear to be more widely known in the physical chemistry literature and have been discussed for some time. See, for example, de Heer^[4] and Liu, *et al.*,^[5] for an historical account of Le Chatelier's principle.)

Consider, for example, the ammonia synthesis reaction

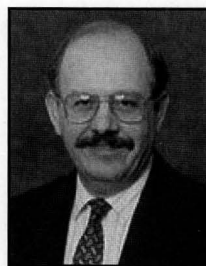
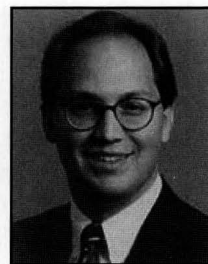


in which equilibrium has been established at a given tem-

perature, T, and pressure, P. Le Chatelier's principle predicts that the reaction will shift to the right (*i.e.*, more ammonia will be produced) upon the addition of more nitrogen to the reaction vessel. If the initial mole fraction of nitrogen exceeds 0.5 and the given T and P are held fixed, however, the reaction instead proceeds to the left, producing more nitrogen, as predicted from rigorous equilibrium constant calculations (the value of 0.5, as shown later, is calculated assuming ideal gas behavior). This shift to the left is a clear exception to the principle of Le Chatelier, which has not been rigorously proven^[4]

Proofs of this unexpected shift have been given before.^[4-6] Most chemical engineering texts do not provide a proof, except, for example, Tester and Modell,^[3] which does provide a detailed proof. The most widely referenced and reproduced proof is by Katz^[6] (the procedure followed in Liu, *et al.*,^[5] is nearly the same as the approach by Katz, although the au-

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To address the technical and educational issues of Le Chatelier's principle, we therefore present in this paper a new and conceptually more straightforward analysis of the direction of the equilibrium shift for the ammonia synthesis reaction as an example.

thors were apparently unaware of Katz). This proof makes use of a "reaction quotient" that has the same functional form as the ratio of mole fractions at equilibrium and is applicable whether or not equilibrium has been established. The value of this reaction quotient, defined in Eq. (3), varies if a change occurs, but must equal the equilibrium constant when the system returns to an equilibrium state. The direction that the reaction quotient takes to restore itself to the equilibrium value determines the direction of reaction for the given change.

The use of a reaction quotient can be confusing to students, particularly to students exposed to reaction equilibria for the first time. To address the technical and educational issues of Le Chatelier's principle, we therefore present in this paper a new and conceptually more straightforward analysis of the direction of the equilibrium shift for the ammonia synthesis reaction as an example. Our approach is, however, more general. In contrast to the other methods, changes at constant T and P are now considered in which the value of the reaction quotient is strictly held fixed and equal to the equilibrium constant. Hence, the analysis makes no use of a separately defined reaction quotient (that is applicable whether equilibrium is or is not established) and should be easier for students to understand. The analysis also involves finite, as well as infinitesimal, changes, which can be the basis of future experimental tests that may demonstrate more vividly the key thermodynamic laws (see del Pino, *et al.*,^[7] for an example of a simple experiment concerning shifts of chemical equilibrium).

Le Chatelier's principle can be reformulated in a more general way that becomes universally valid,^[4,5] although it bears little resemblance to the statement given earlier. For pedagogical reasons, we briefly discuss this new general statement in the last section of this paper. An excellent overview, and proof, of this new general statement is given by de Heer.^[4] It is, however, only valid for *infinitesimal* changes from the initial equilibrium state.^[5] In this paper, we also consider the ammonia synthesis reaction for the case of adding nitrogen in finite amounts (Liu, *et al.*,^[5] considered finite additions as well, but the present analysis provides a more straightforward and quantitative discussion). The value of 0.5 for the mole fraction of nitrogen, above which the reaction proceeds to the left while below the reaction proceeds to the right, is shown to be true for infinitesimal additions of nitrogen.

For *finite* changes, no universally valid statement on the direction in which the reaction shifts can be formulated, and thus each case must be considered individually. In such cases,

instructors should advise ignoring the reformulated Le Chatelier's principle and instead should calculate, in general, the shift in the equilibrium state directly from the relations of chemical equilibrium.

AMMONIA SYNTHESIS REACTION

Exception to the Principle of Le Chatelier

Let us consider the ammonia synthesis reaction and assume for simplicity that the components comprise an ideal-gas mixture. Analyses for nonideal mixtures, although possible, have not been reported. Let species 1 represent nitrogen, species 2 hydrogen, and species 3 ammonia. The chemical potential of each species *i*, $\hat{\mu}_i$, in the ideal-gas mixture is given by^[8]

$$\hat{\mu}_i = \Gamma_i(T) + RT \ln y_i P \quad (1)$$

where $\Gamma_i(T)$ is the chemical potential of pure component *i*, as an ideal gas, at the temperature *T* (and a fixed reference pressure P_o), *R* is the ideal gas constant, *P* is the system pressure, and y_i is the mole fraction of species *i*. At equilibrium, the chemical potentials of the components participating in the chemical reaction must satisfy^[3]

$$\sum_i v_i \hat{\mu}_i = 0 \quad (2)$$

where v_i is the stoichiometrically balanced coefficient of species *i* in the reaction ($v_1 = -1$, $v_2 = -3$, $v_3 = 2$). Upon substituting Eq. (1) into Eq. (2), rearrangement yields

$$\frac{y_3^2}{y_1 y_2^3} = P^2 K(T) = K_p(T, P) \quad (3)$$

where *K*(*T*) is the equilibrium constant and $K_p(T, P)$ is a function of *T* and *P*. The ratio of mole fractions on the far left side of Eq. (3) is the "reaction quotient."

Now, let the system be at equilibrium at a given *T* and *P*. At the initial equilibrium state, there are n_1^o , n_2^o , and n_3^o moles of each species with mole fractions y_1^o , y_2^o , and y_3^o satisfying Eq. (3). Next, we consider the addition of Δ moles of nitrogen (1), while keeping *T* and *P* constant. As the system re-equilibrates, the reaction proceeds so that the final mole numbers of each species will be given by^[8]

$$\begin{aligned} n_1 &= n_1^o + \Delta - \xi \\ n_2 &= n_2^o - 3\xi \\ n_3 &= n_3^o + 2\xi \end{aligned} \quad (4)$$

where ξ is the extent of reaction starting from the above initial equilibrium state; ξ is defined to be positive if the reaction proceeds to the right, *i.e.*, nitrogen and hydrogen are consumed while ammonia is produced, and negative if the reaction proceeds to the left. The above relations imply that the final mole fractions are given by

$$\begin{aligned} y_1 &= \frac{n_1^0 + \Delta - \xi}{n^0 + \Delta - 2\xi} = \frac{y_1^0 + \Delta' - \xi'}{1 + \Delta' - 2\xi'} \\ y_2 &= \frac{y_2^0 - 3\xi'}{1 + \Delta' - 2\xi'} \\ y_3 &= \frac{y_3^0 + 2\xi'}{1 + \Delta' - 2\xi'} \end{aligned} \quad (5)$$

where $n \equiv n_1^0 + n_2^0 + n_3^0$, $\Delta' \equiv \Delta / n^0$, and $\xi' \equiv \xi / n^0$; Δ' and ξ' are dimensionless quantities. Since T and P are held constant, Eq. (3) implies that

$$\frac{(y_3^0 + 2\xi')^2 (1 + \Delta' - 2\xi')^2}{(y_1^0 + \Delta' - \xi')(y_2^0 - 3\xi')^3} = K_p(T, P) = \frac{(y_3^0)^2}{y_1^0 (y_2^0)^3} \quad (6)$$

Equation 6 is valid for all values of Δ' and can be used to determine the value of ξ' for a given choice of Δ' . The sign of ξ' , however, determines the direction in which the reaction shifts, and its value determines the extent of the reaction triggered by the addition of nitrogen.

First, we focus on how the extent of the reaction varies when an infinitesimal amount of nitrogen, *i.e.*, $\Delta' \rightarrow 0$, is added. One can solve Eq. (6) for various values of Δ' and then determine the sign of ξ' as $\Delta' \rightarrow 0$. But since $\xi' \rightarrow 0$ as $\Delta' \rightarrow 0$, we instead determine $d\xi' / d\Delta'$ analytically for $\Delta' \rightarrow 0$. To proceed, and for ease of further manipulations, we first rewrite Eq. (6) as

$$\begin{aligned} (y_3^0 + 2\xi')^2 (1 + \Delta' - 2\xi')^2 y_1^0 (y_2^0)^3 = \\ (y_3^0)^2 (y_1^0 + \Delta' - \xi')(y_2^0 - 3\xi')^3 \end{aligned} \quad (7)$$

We now differentiate both sides of Eq. (7) with respect to Δ' for constant y_1^0 , y_2^0 , and y_3^0 , letting $\eta \equiv d\xi' / d\Delta' = d\xi / d\Delta$. We then take the limit for $\Delta' \rightarrow 0$, with $\xi' \rightarrow 0$ as well, and finally solve for η . After a few lines of algebra, we obtain

$$\eta = \frac{d\xi}{d\Delta} = \frac{y_3^0 y_2^0 (1 - 2y_1^0)}{4y_1^0 y_2^0 (1 - y_3^0) + y_2^0 y_3^0 + 9y_1^0 y_3^0} \quad (8)$$

Since the denominator in Eq. (8) is always positive, the sign of η is given by the sign of $(1 - 2y_1^0)$. Therefore, for infinitesimal additions of nitrogen, we conclude that

when $y_1^0 < \frac{1}{2}$, $\eta > 0$:

*reaction proceeds to the right,
consistently with the Le Chatelier Principle* (9a)

when $y_1^0 > \frac{1}{2}$, $\eta < 0$:

*reaction proceeds to the left,
against the Le Chatelier Principle* (9b)

when $y_1^0 = \frac{1}{2}$, $\eta = 0$:

*no reaction takes place,
against the Le Chatelier Principle* (9c)

Hence, the exception to Le Chatelier's principle occurs when the initial equilibrium mole fraction of nitrogen is equal to or exceeds 0.5 and is independent of the mole fractions of the other species or of the values of the temperature and pressure.

Why the reaction reverses direction can be understood qualitatively^[1] by considering the form of the reaction quotient in Eq. (3). The addition of nitrogen increases the mole fraction of nitrogen, y_1 , but also causes a decrease in y_2 (hydrogen) and y_3 (ammonia). Since y_2 is cubed in the denominator of the reaction quotient, the decrease in y_2 may have a more significant effect on the reaction quotient than the increase in y_1 or decrease in y_3 . When the mole fraction of nitrogen is small, the change in y_1 upon addition of some nitrogen yields a proportionally larger change in y_1 as compared to the decreases in y_2 and y_3 . To compensate, and so ensuring that the reaction quotient must remain equal to $K_p(T, P)$, the reaction proceeds to the right, reducing some of the added nitrogen and producing more ammonia. When the mole fraction of nitrogen is large, so that the mole fraction of hydrogen is small, the proportional decrease in y_2 is greater than the increase in y_1 . The decrease in y_2 is magnified by the appearance of y_2^3 , and so the reaction proceeds to the left, generating more nitrogen and

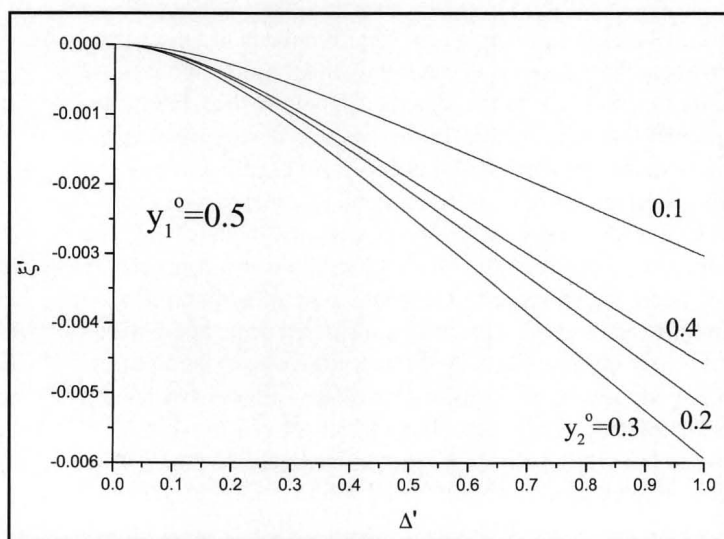


Figure 1. Extent of reaction versus the amount of nitrogen added for $y_1^0 = 0.5$.

hydrogen (thereby offsetting, to some degree, the decrease in y_2). Why the reaction shifts direction when y_1 exceeds 0.5 is, however, not readily apparent from the above analysis. The composition at which the reaction changes direction is, in general, dependent on the form of the reaction quotient.^[6]

The above exceptions, relations (9b) and (9c), do not occur when hydrogen or ammonia are added to the system or when the temperature and volume are held constant.^[1,6] The addition of an inert species does not alter these conclusions. Many other reactions can exhibit such exceptions to Le Chatelier's principle, including liquid-phase reactions. Katz^[6] considers in general the conditions under which a reaction with several reactants and products shifts to the left. The results depend on the stoichiometric coefficients of the given species and can be analyzed similarly as above. Such examples can provide useful teaching assignments, and use of

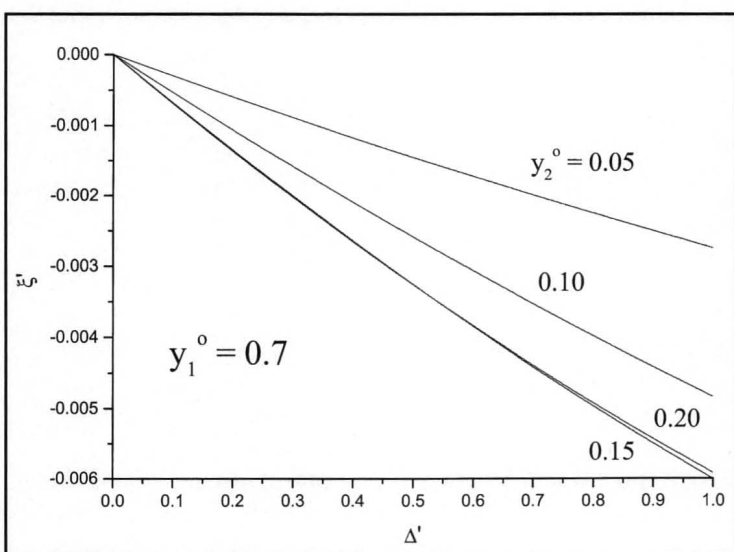


Figure 2. Extent of reaction versus the amount of nitrogen added for $y_1^o = 0.7$.

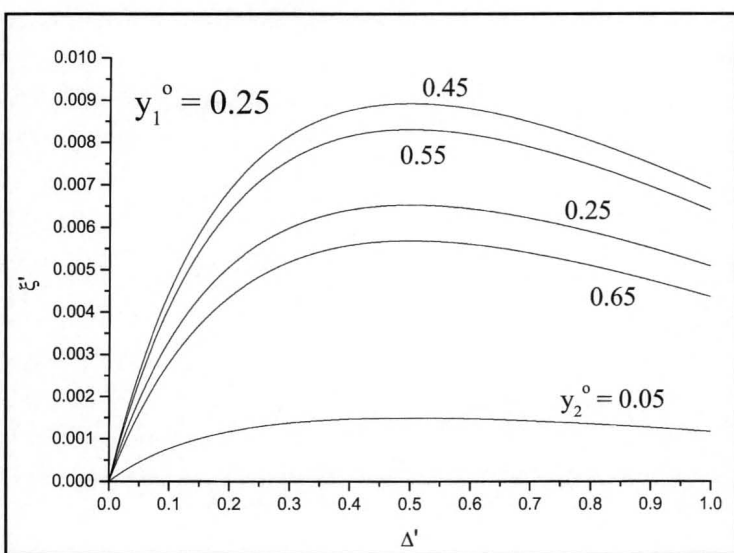


Figure 3. Extent of reaction versus the amount of nitrogen added for $y_1^o = 0.25$.

nonideal gas models may provide further enrichment.

Equation (8) and the conclusions of (9) are valid only for infinitesimal additions of nitrogen at constant T and P. Equation (6) or (7), however, is valid for finite additions of nitrogen at fixed T and P. To determine how the reaction shifts upon addition of a finite amount of nitrogen, one must use Eq. (6) or (7) to determine the value (and sign) of ξ' for a given value of Δ' . Given that $y_3^o = 1 - y_1^o - y_2^o$, Eq. (7) can be rewritten as

$$\begin{aligned} & (1 - y_1^o - y_2^o + 2\xi')^2 (1 + \Delta' - 2\xi')^2 y_1^o (y_2^o)^3 \\ & = (1 - y_1^o - y_2^o)^2 (y_1^o + \Delta' - \xi') (y_2^o - 3\xi')^3 \quad (10) \end{aligned}$$

This equation is fourth-order in ξ' with roots that depend on Δ' , y_1^o , and y_2^o . The physically relevant value of ξ' must be such that each of the terms in parentheses in Eq. (10) and the final mole fractions of Eq. (5) lie between 0 and 1. For small to moderate values of Δ' , the physically relevant solution of Eq. (10) is therefore small. Equation (10) was solved by the standard Newton-Raphson's method with an initial guess of $\xi' = 0$. Convergence to the one physical root was readily achieved. Values of ξ' were generated for a range of Δ' at a given y_1^o and y_2^o . One may vary y_2^o independently from y_1^o , with the constraint that $0 < y_2^o < 1 - y_1^o$. Equation (10), like Eqs. (6) and (7), also does not require that one specify the pressure and temperature explicitly. The value of y_2^o for a given y_1^o must be consistent with the choice of T and P in Eq. (3), but the specific value of T and P is not required for the determination of ξ' .

Figure 1 displays a plot of ξ' versus Δ' for $y_1^o = 0.5$ and different values of y_2^o . In all cases, $\xi' \rightarrow 0$ as $\Delta' \rightarrow 0$, and the slope of ξ' approaches zero as $\Delta' \rightarrow 0$, consistent with relation (9c). Nonetheless, for any finite addition of nitrogen, the reaction proceeds to the left, *i.e.*, $\xi' < 0$. The value of ξ' is quite small, remaining so as $\Delta' \rightarrow 1$. The reaction proceeds to the left, but only by a relatively small extent, even if nitrogen is added in an amount equal to the total number of moles of all the species initially present (*e.g.*, $\xi' \approx -0.006$ for $\Delta' = 1.0$ and $y_2^o = 0.30$). The extent of reaction, though always negative, also depends on y_2^o .

Figures 2 and 3 display plots of ξ' versus Δ' for $y_1^o = 0.7$ and $y_1^o = 0.25$, respectively, at different values of y_2^o . When $y_1^o = 0.7$, the limiting slopes are all negative, consistent with relation (9b), and a finite addition of nitrogen, at least up to $\Delta' = 1$, causes the reaction to proceed to the left ($\xi' < 0$). When $y_1^o = 0.25$, the limiting slopes are all positive, again as required by relation (9a), and a finite addition of nitrogen up to $\Delta' = 1$ causes the reaction to proceed to the right ($\xi' > 0$). Yet, the curves in Figure 3 display maxima, suggesting that for suffi-

ciently large Δ' , the curves will eventually yield negative values of ξ' .

To illustrate this effect further, we consider Figure 4 in which $y_1^o = 0.45$. As required by relation (9a), all the curves initially have a positive slope, so that the reaction proceeds to the right for small values of Δ' . At some critical value of Δ' (which depends slightly on y_2^o), ξ' becomes negative. Therefore, at $y_1^o = 0.45$, the reaction proceeds to the right for small additions of nitrogen, but shifts to the left when a sufficient quantity of nitrogen is added. The figures suggest that for all values of y_1^o , the reaction will eventually proceed to the left if a large enough amount of nitrogen is added to the reaction vessel. These calculations also suggest ways for experimentally testing the predictions and demonstrating the thermodynamic laws.

GENERALIZATION OF LE CHATELIER'S PRINCIPLE

The Principle of Moderation

We close this paper by briefly discussing the generalized statement of Le Chatelier as stated and proved by de Heer,^[4] which is more appropriately called a Principle of Moderation (the proof given by de Heer is beyond the scope of an undergraduate course). Since generality often causes one to sacrifice simplicity, the more general principle of moderation may be given as^[4]

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

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

The above statement has been shown to be valid only for infinitesimal changes from the initial equilibrium state.^[4,5] It does not necessarily hold for finite changes.^[5]

The principle of moderation applies, for example, to the change of the chemical potential of nitrogen (intensive variable) upon the addition of nitrogen (conjugate extensive variable). With the ammonia synthesis reaction prevented from occurring, the addition of nitrogen at constant T and P yields an increase in the value of the chemical potential of nitrogen. If nitrogen were instead added while maintaining chemical equilibrium, *i.e.*, the reaction was allowed to proceed, the resultant increase in the chemical potential of nitrogen would be smaller

than the increase obtained when the reaction was prohibited. In other words, the change in the chemical potential of nitrogen is moderated, or lessened in this example, by the reaction.

Since at constant T and P the chemical potential of a component in an ideal-gas mixture increases with increasing mole fraction, we instead analyze the change in the mole fraction of nitrogen upon the addition of nitrogen to illustrate in more detail the principle of moderation (this is one aspect of the ammonia synthesis reaction that was not directly discussed by de Heer). We consider the addition of nitrogen with the ammonia synthesis reaction taking place and with the reaction prevented from occurring. From Eq. (5), we see that in the limit of $\Delta' \rightarrow 0$

$$\frac{dy_1}{d\Delta'} = 1 - y_1^o + \eta(2y_1^o - 1) \quad (11)$$

If no reaction is allowed to take place, then the final mole fraction of y_1 is equal to

$$y_1 = \frac{y_1^o + \Delta'}{1 + \Delta'} \quad (12)$$

Taking the derivative of y_1 with respect to Δ' , we find in the limit of $\Delta' \rightarrow 0$ that

$$\left(\frac{dy_1}{d\Delta'}\right)_{\text{no rxn}} = 1 - y_1^o > 0 \quad (13)$$

Equations (11) and (13) imply that

$$\frac{dy_1}{d\Delta'} = \left(\frac{dy_1}{d\Delta'}\right)_{\text{no rxn}} + \eta(2y_1^o - 1) \quad (14)$$

Since Eq. (8) indicates that $\eta(2y_1^o - 1) \leq 0$, then

$$\frac{dy_1}{d\Delta'} \leq \left(\frac{dy_1}{d\Delta'}\right)_{\text{no rxn}} \quad (15)$$

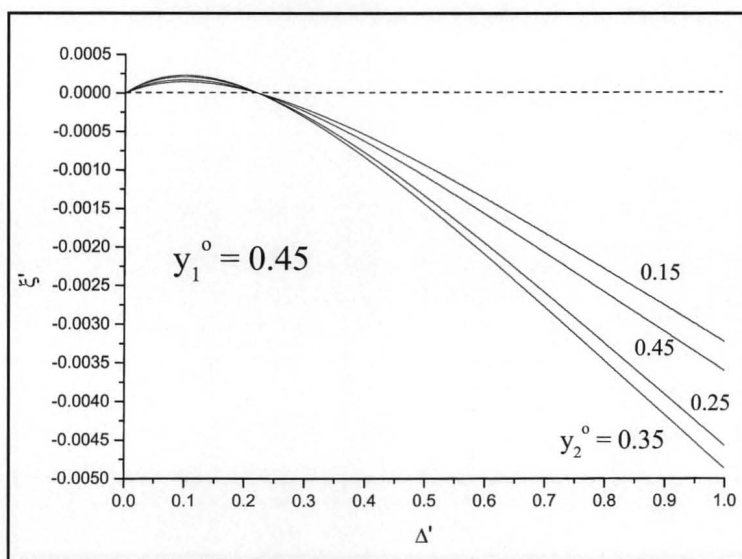


Figure 4. Extent of reaction versus the amount of nitrogen added for $y_1^o = 0.45$.

or the change in the mole fraction of nitrogen is always less (or equal) when the reaction proceeds than when no reaction takes place. The reaction is said to "moderate" the mole fraction of nitrogen, *i.e.*, the reaction decreases the final mole fraction of nitrogen as compared to the case when no reaction occurs. This result is counter-intuitive, since Eq. (15) is also valid when the reaction shifts to the left, thereby producing more nitrogen. In this instance, the additional hydrogen that is produced by the reaction shifting to the left offsets the increase in the mole fraction of nitrogen.

Similar arguments, as discussed by de Heer, show that the partial pressure and chemical potential of nitrogen are also moderated by the reaction: the change in these intensive quantities is always less when the reaction occurs than when no reaction takes place. Equation (15) also supports these conclusions since, at constant T and P, the partial pressure and chemical potential of a component in an ideal gas mixture increase with increasing mole fraction.

For finite additions of nitrogen, and for most conditions, calculations show that Eq. (15) is still satisfied. There are ranges of finite Δ' , however, in which the reaction does not moderate the change in mole fraction of nitrogen (a value of $y_1^\circ = 0.45$ provides an example for Δ' between approximately 0.12 and 0.22). In this case, the final mole fraction of nitrogen after reaction is in fact greater than the final mole fraction of nitrogen without reaction. The ratio of the final mole fraction of nitrogen with reaction to the mole fraction without reaction is, however, only slightly greater than unity. Thus, in this case, the violation of the principle is minor for finite values of Δ' .

CONCLUSIONS

When a gas-phase system is at chemical reaction equilibrium at constant temperature and pressure, and some extra reactant or product is added, the system, upon reestablishing equilibrium does not always respond in a way qualitatively consistent with the traditional Le Chatelier principle. If there is a change in the number of moles, as in the ammonia synthesis reaction, then adding one reactant (N_2) may cause the reaction to proceed in a direction that produces more of the added ingredient (N_2). These results are perfectly consistent with the laws of thermodynamics. The direction of the reaction depends on whether the added amount is infinitesimal or finite. For infinitesimal additions, a new principle of mod-

eration, first suggested formally by de Heer,^[4] does apply. Even this principle does not apply for finite additions of reactant (N_2). These results indicate that the principle of Le Chatelier should be taught in its more general form. In addition, instructors should emphasize that even the more general formulation is valid for infinitesimal changes only. (Nonetheless, the principle does appear to be valid for finite changes in temperature and pressure.) The present analysis provides for a deeper understanding of chemical reaction equilibria and can form the basis of several stimulating lectures and problem-solving sessions.

As a final note, a general statement concerning the direction of shift for changes in temperature of arbitrary amounts at constant pressure can be formulated. Assuming that the heat of reaction is always positive or negative, then an increase in temperature of any amount will cause the equilibrium to be displaced in the direction of the heat of reaction. A similar statement appears to be possible for pressure changes at constant temperature and depends on which direction the volume changes upon reaction. The addition of reactants and/or products, however, requires care, and in these cases it is not possible to formulate a general statement that is universally valid for any addition of products or reactants.

The present analysis provides for a deeper understanding of chemical reaction equilibria and can form the basis of several stimulating lectures and problem-solving sessions.

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