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The Conditions of the Violations of Le Chatlier's Principle in Gas Reactions at Constant T and P

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| ARTICLE INFO	ABSTRACT
	Le Chatelier's principle is used as a very simple way to predict the effect of a change in conditions on a chemical equilibrium. However, several studies have been reported the violation of this principle, still there is no reported simple mathematical equation to express the exact condition of violation in the gas phase reactions. In this article, we derived a simple equation for the violation of Le Chatelier's principle for the ideal gas reactions at the constant temperature and pressure.

1. INTRODUCTION AND PRELIMINARIES

Le Chatelier principle (LCP) is a very simple way of predicting the direction of a disturbed chemical equilibrium [1]. LCP is often expressed as follows: 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 of that variable. However, the LCP has led to some wrong predictions and thus caused to some controversial discussions among many students and teachers [2−7].

The industrial synthesis of ammonia is shown below:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
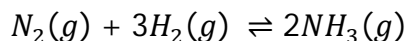
This is a traditional example used by teachers when the LCP is discussed. In this reaction, at constant pressure and temperature, when the mole fraction of nitrogen in the equilibrium mixture exceeds 0.5, the LCP predicts that this change should shift the equilibrium to the right in order to moderate the excess of nitrogen. However, in contrast to LCP prediction this disturbance shifts the reaction to the left, producing more N_2.

Although many discussions and examples of the failure of LCP have been reported, a simple inquiry to predict the conditions of the failure of LCP in gas phase reaction (at constant T and P) is still missing. The inquiries discussed by Jeffrey E. Lacy [10] are not general and only limited to special cases, where $\Delta v < 0$.

In this work, we mathematically derive the criteria in which LCP fails to predict the correct direction of a reaction at equilibrium upon changing the mole number of a species at constant T and P.

2. THEOREM AND DERIVATION

Theorem 1. In the ideal gas reaction $\sum_i v_i A_i(g) = 0$ where $\frac{\Delta n}{mol} = \sum_i v_i$ and v_i is the stoichiometric factor of species $A_i(g)$ in the reaction (where it is positive for products and negative for reactants). At constant temperature (T) and pressure (P), by changing n_j of the j-th species, the reaction proceeds towards the direction that offsets this perturbation unless: $x_j \geq \left|\frac{v_j}{\Delta n}\right| mol$ and $\Delta n \neq 0$, where, x_j is the mole fraction of j-th species at the reaction equilibrium before perturbation. In equal st ate, the reaction equilibrium does not change. However, in non-equal state, the perturbation factor is elevated.

Derivation 2. The expression for the chemical potential (μ_i) at equilibrium is given as $\sum v_i \mu_i = 0$. This term leads to $\Delta G^0 = RT ln K_p^0$, where $\Delta G^0 = \sum v_i \mu_i^0$ and the standard equilibrium constant $K_P^0 = \prod_i (P_i/P_0)^{v_i}$ is a function of T only.

For a closed system in equilibrium (at constant P and T), if we perturb the system by adding (or removing) n_i mole of A_j, the equilibrium will shift to the direction to counteract this perturbation. Because in this condition K_{eq} is constant, we use Q_p as a parameter to find the direction of shift. We know from thermodynamic if $Q_p < K_{eq}$, the reaction proceeds forward (producing more product) and if $Q_p > K_{eq}$, the reaction proceeds backward (producing more reactant). At constants T and P, Q depend only on $n_j Q_P = Q_P(n_1, n_2, \dots, n_j \dots)$. Let us add small mole of A_j (dn_j) to this system. The term $\frac{\partial Q_P}{\partial n_j}$ represents the change in Q_p upon addition of A_j. As dn_j is positive, the sign of dQ_P illustrates the direction of reaction. The term $dQ_P > 0$ denotes the elevation of Q_p upon addition of species. This is the case where reaction proceeds backward to reach the new equilibrium (because K_{eq} is constant). In the same way, the reaction proceeds forward if $dQ_P < 0$. However, there is no change in the reaction equilibrium upon addition of n_j if $dQ = 0$. Before going step forward to the final statement, let us discuss the following required expressions:

$$\frac{\Delta n}{mol} = \sum_i v_i \tag{1}$$

$$Q_P = \prod_i (P_i)^{\nu_i} \tag{2}$$

$$P_i = x_i P \tag{3}$$

$$x_i = \frac{n_i}{n_t} \tag{4}$$

$$n_t = \sum_i n_i \tag{5}$$

where in these equations, P_i, x_i, and n_i are partial pressure, mole faction, and mole numbers of A_i, respectively. The n_t is the total mole numbers of all gases in the reaction. By substituting the equations 1, 3, 4 into Eq. 2, we get:

$$
\begin{aligned}
Q_P &= \prod_i (P_i)^{\nu_i} = \prod_i (x_i P)^{\nu_i} \\
&= \left(\prod_i (x_i)^{\nu_i}\right)\left(\prod_i (P)^{\nu_i}\right) \\
&= \left(\prod_i \left(\frac{n_i}{n_t}\right)^{\nu_i}\right)\left((P)^{\Sigma_i \nu_i}\right) \\
&= \left(\frac{\prod_i (n_i)^{\nu_i}}{\prod_i (n_t)^{\nu_i}}\right)\left((P)^{\frac{\Delta n}{mol}}\right) \\
&= \left(\frac{\prod_i (n_i)^{\nu_i}}{(n_t)^{\Sigma_i \nu_i}}\right)(P)^{\frac{\Delta n}{mol}} \\
&= \left(\frac{\prod_i (n_i)^{\nu_i}}{(n_t)^{\frac{\Delta n}{mol}}}\right)P^{\frac{\Delta n}{mol}} \\
&= P^{\frac{\Delta n}{mol}} n_t^{-\frac{\Delta n}{mol}} \prod_i (n_i)^{\nu_i}
\end{aligned}
\tag{6}
$$

The final statement is used to obtain $\left(\dfrac{\partial Q_P}{\partial n_j}\right)_{T,P,n_{i \neq j}}$

$$
\begin{aligned}
\left(\frac{\partial Q_P}{\partial n_j}\right)_{T,P,n_{i \neq j}} &= \left(\frac{\partial}{\partial n_j}\right)_{T,P,n_{i \neq j}}\left[P^{\frac{\Delta n}{mol}} n_t^{-\frac{\Delta n}{mol}}(\prod_i (n_i)^{\nu_i})\right] = P^{\frac{\Delta n}{mol}}\left(\frac{\partial}{\partial n_j}\right)_{T,P,n_{i \neq j}}\left[n_t^{-\frac{\Delta n}{mol}}(\prod_i (n_i)^{\nu_i})\right] \\
&= P^{\frac{\Delta n}{mol}}\left[\left(-\frac{\Delta n}{mol}\right)\left((n_t)^{-\frac{\Delta n}{mol}-1}\right)(\prod_i (n_i)^{\nu_i}) + \left((n_t)^{-\frac{\Delta n}{mol}}\right)(\nu_j)\left((n_j)^{\nu_j-1}\right)(\prod_{i \neq j}(n_i)^{\nu_i})\right] \\
&= P^{\frac{\Delta n}{mol}}\left[\left(-\frac{\Delta n}{mol}\right)\left(\frac{(n_t)^{-\frac{\Delta n}{mol}}}{n_t}\right)(\prod_i (n_i)^{\nu_i}) + \left((n_t)^{-\frac{\Delta n}{mol}}\right)(\nu_j)\left(\frac{(n_j)^{\nu_j}}{n_j}\right)(\prod_{i \neq j}(n_i)^{\nu_i})\right] \\
&\times \left(\frac{P}{n_t}\right)^{\frac{\Delta n}{mol}}\left[\left(-\frac{\Delta n}{mol}\right)\frac{1}{n_t}\prod_i (n_i)^{\nu_i} + (\nu_j)\frac{1}{n_j}\prod_i (n_i)^{\nu_i}\right] \\
&= \left(\frac{P}{n_t}\right)^{\frac{\Delta n}{mol}}\prod_i (n_i)^{\nu_i}\left[\left(-\frac{\Delta n}{mol}\right)\frac{1}{n_t} + (\nu_j)\frac{1}{n_j}\right]
\end{aligned}
\tag{7}
$$

By Eq. 4 into the final term of Eq. 7, we have:

$$x_j = \frac{n_j}{n_t} \rightarrow n_t = \frac{n_j}{x_j}$$

$$\left(\frac{\partial Q_P}{\partial n_j}\right)_{T,P,n_{i\neq j}} = \left(\frac{P}{n_t}\right)^{\frac{\Delta n}{mol}} \prod_i (n_i)^{v_i} \left[-\frac{\Delta n}{mol}\frac{1}{n_j/x_j} + \frac{v_j}{n_j}\right]$$

$$= \left(\frac{P}{n_t}\right)^{\frac{\Delta n}{mol}} \prod_i (n_i)^{v_i} \left[-\frac{\Delta n}{mol}\frac{x_j}{n_j} + \frac{v_j}{n_j}\right] = \left(\frac{P}{n_t}\right)^{\frac{\Delta n}{mol}} \left(\frac{\prod_i(n_i)^{v_i}}{n_j}\right) \left[v_j - x_j\frac{\Delta n}{mol}\right]$$

(8)

The statement before bracket is denoted as ω for simplicity. It is clear that this statement is positive.

$$\left(\frac{P}{n_t}\right)^{\frac{\Delta n}{mol}} \left(\frac{\prod_i(n_i)^{v_i}}{n_j}\right) \equiv \omega > 0$$

Now Eq. 8 will be written as:

$$\left(\frac{\partial Q_P}{\partial n_j}\right)_{T,P,n_{i\neq j}} = \omega\left[v_j - x_j\frac{\Delta n}{mol}\right]$$

(9)

$$(\partial Q_P)_{T,P,n_{i\neq j}} = \omega\left[v_j - x_j\frac{\Delta n}{mol}\right](\partial n_j)_{T,P,n_{i\neq j}}$$

(10)

We now assume $(\partial n_j)_{T,P,n_{i\neq j}}$ is positive, which means that n_j is added to the system. Therefore, the only parameter which effects the sign of $(\partial Q_P)_{T,P,n_{i\neq j}}$ is the statement inside the bracket, i.e. $v_j - x_j\frac{\Delta n}{mol}$. We now try to determine the sign of this statement. To do it, let us refer to the absolute property as follows:

$$|\theta| = \begin{cases} +\theta, & \theta > 0 \\ -\theta, & \theta < 0 \end{cases}$$

(11)

We now distribute Eq. 10 vs. sign of v_j and Δn to find in which condition $(\partial Q_P)_{T,P,n_{i\neq j}}$ is positive, negative or zero. For simplicity, we omit subscript T, P and $n_{i\neq j}$.

$$\begin{cases} v_j > 0 \to \partial Q_P = \omega\left[+|v_j| - x_j\frac{\Delta n}{mol}\right]\partial n_j \begin{cases} \Delta n > 0 \to \partial Q_P = \omega\left[+|v_j| - x_j\left|\frac{\Delta n}{mol}\right|\right]\partial n_j \to \begin{cases} |v_j| > x_j\left|\frac{\Delta n}{mol}\right| \to \partial Q_P > 0 \\ |v_j| < x_j\left|\frac{\Delta n}{mol}\right| \to \partial Q_P < 0 \\ |v_j| = x_j\left|\frac{\Delta n}{mol}\right| \to \partial Q_P = 0 \end{cases} \\ \Delta n = 0 \to \partial Q_P = \omega[+|v_j|]\partial n_j > 0 \\ \Delta n < 0 \to \partial Q_P = \omega\left[+|v_j| + x_j\left|\frac{\Delta n}{mol}\right|\right]\partial n_j > 0 \end{cases} \\ v_j < 0 \to \partial Q_P = \omega\left[-|v_j| - x_j\frac{\Delta n}{mol}\right]\partial n_j \begin{cases} \Delta n > 0 \to \partial Q_P = \omega\left[-|v_j| - x_j\left|\frac{\Delta n}{mol}\right|\right]\partial n_j < 0 \\ \Delta n = 0 \to \partial Q_P = \omega[-|v_j|]\partial n_j < 0 \\ \Delta n < 0 \to \partial Q_P = \omega\left[-|v_j| + x_j\left|\frac{\Delta n}{mol}\right|\right]\partial n_j \to \begin{cases} |v_j| > x_j\left|\frac{\Delta n}{mol}\right| \to \partial Q_P < 0 \\ |v_j| < x_j\left|\frac{\Delta n}{mol}\right| \to \partial Q_P > 0 \\ |v_j| = x_j\left|\frac{\Delta n}{mol}\right| \to \partial Q_P = 0 \end{cases} \end{cases} \end{cases}$$

(12)

For conditions 1, 4 and 5 of Eq. 12, where $v_j > 0$ and $Q_P > 0$, by adding more species from products ($v_j > 0$) Q_p increases. Therefore, the reaction shifts backward to reach the equilibrium, which is in agreement with the LCP. The conditions 6, 7 and 8 are

also in agreement with LCP; where by adding more reactants reaction proceeds forward. For conditions 3 and 10, no effect will be appeared by adding n_j while $\partial Q_P = 0$. The condition 2 (where $v_j > 0$ and $\partial Q_P < 0$) reveals that by adding more product to the reaction at equilibrium, the reaction shifts to the right to produce more product, which is in contradiction to the LCP. The situation 9 is also contradictory to the LCP; where by adding more reactant, the reaction shifts to the left. For these conditions we can write:

$$|v_j| < x_j \left|\frac{\Delta n}{mol}\right| \Rightarrow x_j > \left|\frac{v_j}{\Delta n}\right| mol \tag{13}$$

By combining conditions 2, 3, 9 and 10, we obtain:

$$x_j \geq \left|\frac{v_j}{\Delta n}\right| mol \tag{14}$$

This is the equation we were searching for. From this equation we conclude that the term $x_j = \left|\frac{v_j}{\Delta n}\right| mol$ represents the critical mole fraction; where if x_j increases ($x_j > \left|\frac{v_j}{\Delta n}\right| mol$), LCP would be broken. For NH_3 production from N_2 and H_2, Posthumus [8] found that when the system is initially in chemical equilibrium and has more than 50% N_2, the addition of N_2 as reactant would result in an internal reaction forming more reactant at constant T and P. Using Eq. 14 we also found the critical mole fraction as:

$$x_j = \left|\frac{v_j}{\Delta n}\right| mol = \left|\frac{-1}{-2}\right| = \frac{1}{2}.$$

Now, let's obtain a general perquisite for reactions where the LCP is broken. To do so, we use the fundamental property of the mole fraction which cannot be exceeded unity. Hence the first perquisite is as follows:

$$\left|\frac{v_j}{\Delta n}\right| < 1 \tag{15}$$

Using this statement, we will find plenty of reactions where the LCP could be broken.

3. CONCLUSIONS

We achieved a simple term for the situations that LCP fails to predict the correct direction of the reaction change after suffering a perturbation caused by adding species in gas phase reactions at constant T and P. If the term of Eq. 15 is met, the reaction can go toward the direction of added substrate (reactant or product) only if the mole fraction is larger than the critical mole fraction of $\left|\frac{v_j}{\Delta n}\right| mol$ (Eq. 14). As an example in the following reaction:

$$CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$$
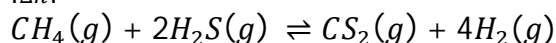
For both $CH_4(g)$ and $CS_2(g)$, *the term* $\left|\frac{v_j}{\Delta n}\right| = \frac{1}{2}$ represents that the first prerequisite is fulfilled, that is $\left|\frac{v_j}{\Delta n}\right| < 1$. In the reaction at equilibrium, if the mole fraction of $CH_4(g)$ or

$CS_2(g)$ is 0.5 or higher, then by adding one of these species to the reaction at constant T and P, the reaction shifts in the direction to produce more of that species, in contradictory to LCP.

Finally, from Eqs. 14 and 15, we also conclude that for the reactions in which Δn is 0 or 1, the LCP will never be broken while v_j is an integer number.

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