

The Scientific Inadequacy of Le Chatelier's Principle

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Introduction

Chemical equilibrium is an important topic in the Hong Kong advanced level chemistry curriculum. Students are expected to have a deep understanding of the concept of dynamic equilibrium. Of particular importance is their ability to predict the effects of changing conditions on the position of chemical equilibrium. For Hong Kong students, the Le Chatelier's principle (LCP) has become an indispensable aid when making such predictions. Le Chatelier first formulated the principle in 1884 (Le Chatelier, 1884), but he himself did not keep to one statement. As a result, different textbook writers may state the principle in different forms. Two examples are shown below:

Le Chatelier's principle states that if a system in equilibrium is subjected to a change (concentration, pressure or temperature), the equilibrium position of the system will shift in a way to minimize the effect of the change. (Wong & Wong, 2003, p. 113)

If a system in equilibrium is subjected to a change, the processes which take place are such as to tend to counteract the effect of the change. (Tong, 1995, p. 306)

Research has confirmed that students often misuse LCP when they solve chemical equilibrium problems (Furio et al., 2000; Quilez-Pardo & Solaz-Portoles, 1995; Tyson, Treagust & Bucat, 1999; Voska & Heikkinen, 2000; Wheeler & Kass, 1978). Some teachers blame students for their misapplication of LCP. However, LCP itself is faulty; there are cases where application of LCP may lead to incorrect predictions (Allsop & George, 1984; Bridgart & Kemp, 1985; de Heer, 1957; Gold & Gold, 1984; Katz, 1961; Kemp, 1987; Posthumus, 1933; Solaz & Quilez, 2001; Solaz-Portoles & Quilez-Pardo, 1995). Unfortunately, few chemistry teachers in Hong Kong are aware of the inadequacy of LCP. Space limitation precludes a discussion of all these cases here. The purpose of this paper is to show four cases so as to help chemistry teachers develop a heightened awareness of the inadequacy of LCP. Ways to improve the teaching and learning of chemical equilibrium at the advanced level are also discussed.

Conflicting Predictions from Le Chatelier's Principle

Case 1: Adding an inert gas to a gaseous equilibrium mixture at constant volume and temperature

For example, consider the following equilibrium problem:

The reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ is at equilibrium in an empty reactor. What will happen if some argon (an inert gas) is added to the equilibrium mixture at constant volume and temperature?

Many textbook writers (e.g., Tong, 1995; Wong & Wong, 2003) argue that the addition of an inert gas increases the total pressure of the system but has no effect on either the concentrations or the partial pressures of the reactants or the products. Therefore, the equilibrium position of the system will not be changed. However, it is important to note that the total pressure has really been increased. According to LCP, the system should adjust itself in such a way that this increase in pressure will be minimized and this can be achieved by shifting the equilibrium position to the reactant side, forming more $\text{PCl}_5(\text{g})$.

Case 2: Adding an inert gas to a gaseous equilibrium mixture at constant pressure and temperature

Some teachers emphasize that the addition of an inert gas *never* disturbs the equilibrium position of a chemical system because there is no reaction between the inert gas and any of the chemicals involved in the forward and reverse reactions. Let us take a look at the following example:

The reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ is at equilibrium in an empty reactor fitted with a movable piston. What will happen if some argon (an inert gas) is added to the equilibrium mixture at constant pressure and temperature?

Actually, the **argon** gas will disturb the equilibrium position of $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$. Even worse, application of LCP will result in conflicting predictions. Because the system is kept at constant pressure and temperature, the argon gas will increase the total volume of the mixture. The concentrations of all gaseous reactants and products will reduce and according to LCP, different directional effects on the equilibrium must result. Thus, LCP fails to give a definite prediction if the number of moles of gaseous products in the balanced equation is not equal to the number of moles of gaseous reactants in the balanced equation (e.g., $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$).

Case 3: Adding or eliminating one of the gaseous substances of an equilibrium mixture at constant pressure and temperature

Consider the **Haber** reaction:

The reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ is at equilibrium in an empty reactor fitted with a movable piston. If a small amount of $\text{N}_2(\text{g})$ is added to the equilibrium mixture at constant temperature and pressure, what will happen to the number of $\text{NH}_3(\text{g})$ molecules when equilibrium is re-established?

This is a well-known example to illustrate the scientific inadequacy of LCP. If we mechanically apply LCP, the equilibrium position should shift to the right in order to counteract the effect of increase in $\text{N}_2(\text{g})$. However, **addition** of $\text{N}_2(\text{g})$ will increase the total volume of the system. Instantaneously, the concentration or **partial pressure** of $\text{N}_2(\text{g})$ will increase but the concentration or partial pressure of $\text{H}_2(\text{g})$ will decrease. If we apply LCP, these two changes in concentration or partial pressure must lead to opposite

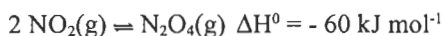
equilibrium shifts. Unfortunately, LCP offers no way of deciding which direction of equilibrium shift will predominate. Thus, there is a possibility that LCP cannot give a definite prediction if the number of moles of gaseous products in the balanced equation is not equal to the number of moles of gaseous reactants in the balanced equation.

Some teachers may argue that LCP fails to give a definite prediction in this case because two kinds of changes are involved and thus the question requires students to solve a complex rather than a simple equilibrium problem. As de Heer (1958) pointed out, changes are never restricted to one variable and multiple changes only constitute a complex process if they are made independent to each other. But adding nitrogen to the $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) = 2\text{NH}_3(\text{g})$ system at constant pressure and temperature is not such a complex change because the volume change involved is entirely determined by the amount of nitrogen added.

Case 4: Changing the temperature of a gaseous equilibrium system at constant volume

Many textbook writers mention the following equilibrium system:

The reaction below is at equilibrium in a sealed flask. If the temperature of the equilibrium mixture is increased, what will happen to the concentration of $\text{N}_2\text{O}_4(\text{g})$ when equilibrium is re-established?



Because the forward reaction is exothermic, LCP predicts that the equilibrium should shift to the left in order to counteract the effect of increase in temperature. However, increasing the temperature will also increase the total pressure of the system. Since there is a decrease in the number of gaseous molecules for the forward reaction, LCP predicts that the equilibrium should shift to the right in order to counteract the effect of pressure increase. Unfortunately, LCP offers no way of deciding which direction of equilibrium shift will predominate. Hence, LCP cannot give a definite prediction if the forward reaction is exothermic and has less gaseous products than gaseous reactants in the balanced equation, or if the forward reaction is endothermic and has more gaseous products than gaseous reactants in the balanced equation.

How to Teach Chemical Equilibrium More Effectively

This section discusses two ways to improve the teaching and learning of chemical equilibrium *without* the use of LCP. The four cases cited in the preceding section are also used as examples. The present discussion is in a form suitable for advanced level chemistry students. Thermodynamic approach and calculus are not used here.

Applying the concept of reaction quotient

The equilibrium constant, K_c , is defined as the product of the *equilibrium concentrations* of the products, each raised to the power that corresponds to its coefficient in the balanced equation, divided by the product of the *equilibrium concentrations* of reactants, each raised to the power that corresponds to its

coefficient in the balanced equation. The reaction quotient, Q , has the same form as the K_c or K_p , but the Q involves specific values that are not necessarily equilibrium values. The reaction quotient for the general reversible reaction, $aA + bB \rightleftharpoons cC + dD$, is given as follows:

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where $[A]$ is the concentration of substance A, and so on.

The values of Q range from 0 (reactants only) to ∞ (products only). If $Q = K$, then the chemical system is at equilibrium. Therefore, we can compare the magnitude of Q with that of K for a system under given conditions to decide whether the forward reaction or the reverse reaction must occur to a greater extent to establish equilibrium. If $Q < K$, the forward reaction must predominate until equilibrium is established. Conversely, if $Q > K$, the reverse reaction must predominate until equilibrium is established.

For Case 1, the K_c for the reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ is calculated as follows:

$$K_c = \frac{\left(\frac{n_{\text{PCl}_3}}{V}\right)\left(\frac{n_{\text{Cl}_2}}{V}\right)}{\left(\frac{n_{\text{PCl}_5}}{V}\right)} = \frac{(n_{\text{PCl}_3})(n_{\text{Cl}_2})}{(n_{\text{PCl}_5})(V)}$$

where V is the total volume, n_{PCl_3} is the number of moles of PCl_3 , and so on.

At equilibrium, the relationship between Q and K is

$$Q_c = \frac{\left(\frac{n_{\text{PCl}_3}}{V}\right)\left(\frac{n_{\text{Cl}_2}}{V}\right)}{\left(\frac{n_{\text{PCl}_5}}{V}\right)} = \frac{(n_{\text{PCl}_3})(n_{\text{Cl}_2})}{(n_{\text{PCl}_5})(V)} = K_c$$

Because adding argon gas at constant volume and temperature will not change the value of any of the terms in the above Q_c expression, there is no change of equilibrium position. Notice that it is not necessary to calculate the exact value of Q in order to make the prediction.

For Case 2, the volume, V , of the system is increased after argon gas is added at constant pressure and temperature.

$$Q_c = \frac{\left(\frac{n_{\text{PCl}_3}}{V}\right)\left(\frac{n_{\text{Cl}_2}}{V}\right)}{\left(\frac{n_{\text{PCl}_5}}{V}\right)} = \frac{(n_{\text{PCl}_3})(n_{\text{Cl}_2})}{(n_{\text{PCl}_5})(V)} < K_c$$

The Q_c has the same form as the K_c expression except that the new value of V should be substituted into the expression. As a result, $Q_c < K_c$ because the denominator of Q_c is larger than that of K_c . To establish equilibrium, the denominator of Q_c must decrease and/or the numerator of Q_c must increase. This can be achieved by decomposing $\text{PCl}_5(\text{g})$ molecules to produce $\text{PCl}_3(\text{g})$ and $\text{Cl}_2(\text{g})$ molecules. So, the forward reaction predominates until equilibrium is re-established. More $\text{PCl}_3(\text{g})$ and $\text{Cl}_2(\text{g})$ molecules will be found in the new equilibrium state. Again, it is not necessary to calculate the exact value of Q in the above analysis.

For Case 3, the K_c expression for the $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$ system is

$$K_c = \frac{(n_{\text{NH}_3} / V)^2}{(n_{\text{N}_2} / V)(n_{\text{H}_2} / V)^3} = \frac{(n_{\text{NH}_3})^2 (V)^2}{(n_{\text{N}_2})(n_{\text{H}_2})^3}$$

At the original equilibrium, we can write

$$Q_c = \frac{(n_{\text{NH}_3} / V)^2}{(n_{\text{N}_2} / V)(n_{\text{H}_2} / V)^3} = \frac{(n_{\text{NH}_3})^2 (V)^2}{(n_{\text{N}_2})(n_{\text{H}_2})^3} = K_c$$

Addition of some nitrogen gas at constant pressure and temperature increases the number of moles of nitrogen, n_{N_2} , in the denominator, but at the same time increases the total volume, V , in the numerator. Therefore, the direction of equilibrium shift will depend on the ratio V^2/n_{N_2} in the Q_c expression. **If the new ratio is larger than the original ratio, then $Q_c > K_c$; equilibrium will shift to the reactant side. If the new ratio is smaller than the original ratio, then $Q_c < K_c$; equilibrium will shift to the product side. In other words, the correct direction of equilibrium shift depends on the initial composition of the $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ mixture.¹**

Applying the van't Hoff equation

The effect of temperature on equilibrium constants can be determined using the van't Hoff equation.²

$$\ln K_p = \text{constant} - \frac{\Delta H^\circ}{RT}$$

where K_p is the equilibrium constant in terms of partial pressures, ΔH° is the standard enthalpy of the forward reaction, R is the molar gas constant, and T is Kelvin temperature. **We can assume that ΔH° for a reaction is independent of temperature. An exothermic reaction has a negative ΔH° , making the second term on the right of this equation positive. As T increases, the second term must decrease, causing K_p to decrease. In contrast, an endothermic reaction has a positive ΔH° , making the second term on the right of the equation negative. As T increases, this term must become less negative, causing K_p to increase. Therefore, according to van't Hoff equation, an increase in temperature at constant pressure or at constant volume**

will cause the equilibrium state of a reversible reaction to shift in the endothermic direction.

For Case 4, the forward reaction of $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ is exothermic. If we increase the temperature of the equilibrium system at constant volume, the equilibrium will shift to the reactant side (i.e., the concentration of $\text{N}_2\text{O}_4(\text{g})$ in the new equilibrium state will decrease). Furthermore, if we plot $\ln K_p$ against $1/T$ for the reaction, the graph should yield a straight line with a slope of $-\Delta H^\circ/R$.

We can write the van't Hoff equation twice, for two different temperatures and with the corresponding equilibrium constants. If we subtract one equation from the other, we should obtain

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Thus, if we know ΔH° and K for a reversible reaction at a given temperature, we can use this form of van't Hoff equation to calculate the value of K at any other temperature. Note that the K in the equation represents K_p . If K_c is given, we have to convert it to K_p before using the equation.³

Concluding Remarks

LCP is deceptively easy to apply to solve chemical equilibrium problems, but there are cases where application of LCP will result in conflicting or incorrect predictions about the effects of changes in concentration, volume, pressure, or temperature on a chemical system at equilibrium. Why does LCP fail to make reliable predictions? The reason is that LCP is ambiguous and scientifically inadequate. Le Chatelier himself never explained the theoretical basis and the limits of applicability of his principle (de Heer, 1957). Since the predictive power of LCP is limited, thermodynamists and chemical educators generally agree that LCP is unimportant for students to understand chemical equilibrium. In other words, LCP is not a pre-requisite to a deep understanding of the concept of chemical equilibrium. If the vision of school chemistry is to present the big ideas in chemistry, then LCP is not a good choice.

A lot of misconceptions held by students have resulted from over-emphasis of LCP. Much of their learning of chemical equilibrium is superficial. It is not appropriate to teach about the limits of applicability of LCP in advanced level chemistry courses because students may feel more confused. The reaction quotient and van't Hoff equations are more powerful than LCP. Unfortunately, most textbook writers in Hong Kong (e.g., Cheng, 1996; Leung & Lee, 2000; Tong, 1995; Wong & Wong, 2003) have not effectively utilized the concept of reaction quotient when they discuss chemical equilibrium problems. They also seldom specify which variables are kept constant. To promote real learning of chemical equilibrium, teachers should emphasize the equilibrium law, the concept of reaction quotient, and the simplified version of van't Hoff equations.

A new advanced level chemistry curriculum will be implemented in Hong Kong in September 2005. To improve the teaching and learning of chemical equilibrium, I have suggested that LCP be deleted from the new curriculum. This is a serious attempt to improve the content of chemistry curriculum in Hong

Kong and teachers should not under-estimate the positive impact of this change on the teaching and learning of chemical equilibrium. However, it must be remembered that innovations in the chemistry curriculum fail to persist unless they are reflected in similar innovations in our public examinations. I hope LCP would not appear in examination questions and mark schemes set by the Hong Kong Examinations and Assessment Authority in future.

Notes:

1. If teachers want to have a deeper understanding of this equilibrium problem, see, for example, Posthumus (1933), Solaz-Portoles and Quilez-Pardo (1995), or Wright (1969). They have proved that if the mole fraction of nitrogen in the original equilibrium mixture is greater than 0.5, restoration of equilibrium will involve decomposition of some ammonia to produce even more nitrogen.
2. Actually, there are two van't Hoff equations. At constant pressure, we have

$$\ln K_p = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

but at constant volume, we need to use

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta U^0}{RT}$$

where ΔS^0 is the standard entropy change for the reversible reaction, R is the molar gas constant, ΔH^0 is the standard enthalpy of the reaction, T is Kelvin temperature, and ΔU^0 is the standard change in internal energy for the system. We can assume that ΔH^0 and ΔS^0 for a reaction is independent of temperature. So, according to van't Hoff equations, an increase in temperature at constant pressure or at constant volume will cause the equilibrium state of a reversible reaction to shift in the endothermic direction.

At constant volume, ΔU^0 should be considered. We can calculate the ΔU^0 for the reversible reaction $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ by the following equation

$$\Delta U^0 = \Delta H^0 - (n_f - n_i)RT.$$

where n_f is the number of moles of gaseous products in the balanced equation and n_i is the number of moles of gaseous reactants in the balanced equation. Assume that T is 100°C (373 K). Thus,

$$\Delta U^0 = \Delta H^0 - (n_f - n_i)RT.$$

$$= -60 \text{ kJ} - (1 \text{ mol} - 2 \text{ mol})(8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(373 \text{ K})$$

$$= -60 \text{ kJ} + 3.1 \text{ kJ}$$

$$= -56.9 \text{ kJ}$$

This calculation shows that the $(n_f - n_i)RT$ term is quite small compared to ΔH^0 . Therefore, ΔU^0 and ΔH^0 are almost the same. But if the ΔH^0 of a particular reaction is close to zero, the sign of ΔU^0 may

change to positive with an increase in temperature. However, this kind of exceptional cases need not be emphasized in advanced level courses.

Hence, for advanced level chemistry courses, there is no need to introduce the van't Hoff equation at constant volume. Because we can assume that ΔH^0 and ΔS^0 for a reaction is independent of temperature, the following form of van't Hoff equation is teachable at advanced level:

$$\ln K_p = \text{constant} - \frac{\Delta H^0}{RT}$$

3. The relationship between K_p and K_c is

$$K_p = K_c (RT)^{(n_f - n_r)}$$

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