

# A mathematical approach to chemical equilibrium theory for gaseous systems IV: a mathematical clarification of Le Chatelier's principle

Ying Liu<sup>1</sup> · Yue Liu<sup>1</sup> · Michael G. B. Drew<sup>2</sup>

Received: 2 December 2014 / Accepted: 3 June 2015 / Published online: 18 June 2015  
© Springer International Publishing Switzerland 2015

**Abstract** Chemical equilibrium is usually discussed via a thermodynamic treatment but this does not automatically provide enough mathematical tools to be successful. A complementary mathematical approach was developed in a series of previous papers to reveal the inner logic in equilibrium shift for gaseous systems. Le Chatelier's principle is reconsidered with this approach and a system has been developed in order to fully address the application of this principle and the dangers of using it without due consideration. In this study it is demonstrated that, more often than not, real conceptual understanding can only be achieved through mathematical derivations which help to build a more rigorous and abstract understanding. The image of chemistry can be improved by introducing more mathematics into elementary chemistry. Real chemical education delves into curricular contents and offers deep insight into chemistry which provides crucial assistance to chemical teachers and benefits students.

**Keywords** Equilibrium theory · Conjugated variables · Equilibrium displacement · Chemical education

---

✉ Yue Liu  
yueliusd@163.com

Ying Liu  
yingliusd@163.com

Michael G. B. Drew  
m.g.b.drew@reading.ac.uk

<sup>1</sup> College of Chemistry and Life Science, Shenyang Normal University, Shenyang 110034, People's Republic of China

<sup>2</sup> School of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK

## 1 Introduction

Le Chatelier's principle provided a remarkable breakthrough in scientific development and continues to have a great influence. Every scientist, whether he is a chemist, physicist, mathematician, or biologist will be familiar with it or its counterparts in the respective fields. For example in biology there is the self-regulatory function of the organism and in physics there are the induced current theorem of Lenz, Newton's first and third laws of motion, which all involve reluctance to change, and both action and reaction. The perceived advantage of Le Chatelier's principle is that it can be used to solve problems without excessive mathematics. Le Chatelier's principle is demonstrated to be "correct" via simple numerical evaluation or elementary mathematical reasoning [1] for chemical systems under constant volume where the principle is less problematic. More theoretical presentations are the thermodynamically derived of Van 't Hoff equation [2,3], and the relationship between Gibbs energy and pressure (Clausius–Clapeyron equation) [4] which are in some ways consistent with Le Chatelier's principle. However thermodynamics itself does not automatically provide enough mathematical tools for the analysis of complicated systems. Several negative effects associated with Le Chatelier's principle [5,6] have been identified [7–12]. The inclusion of Le Chatelier's principle causes problems because it can be, and often is, used in situations for which it is not applicable, especially with gaseous systems at constant temperature  $T$  and pressure  $P$ . Unfortunately it is difficult to predict when the principle is not applicable. Cheung [5] concluded from these negative effects that Le Chatelier's principle was vague and has no value for chemistry other than historical interest. Although we agree with this view to some extent, it is relevant to say that the principle retains relevance but must be used correctly. However, it is relevant to point out here that Le Chatelier's principle creates the prevailing misunderstanding that adding a reactant in a closed system will always displace the chemical equilibrium to reduce the amount of the added reactant and will raise the conversion ratio of other reactants, under any conditions. This is the main concern of the present paper.

Although the problems with the rigor of Le Chatelier's principle have been correctly identified, these problems with Le Chatelier's principle have not been raised in chemistry monographs and indeed student chemistry courses. One reason is that the scientists are often unaware of the achievements of their colleagues [13] and are not aware of, or ignore, published papers that show the failures of Le Chatelier's principle. Still another reason is that most chemists like the style of Le Chatelier's principle because it provides conceptual understanding, albeit flawed [14], without mathematics. Thus, treatments in textbooks often use specific examples with simple mathematical evaluations that give correct answers but which conceal the problems in Le Chatelier's principle. The lacking of theoretical rigor in the treatments make the relevant presentations lack generality. Thus, in order to solve the problems with regard to Le Chatelier's principle, a more general and theoretical presentation for chemical equilibrium is needed to keep up with the level of modern science development. In this work we first present in Sects. 2 and 3 the problems in Le Chatelier's principle and then, in Sect. 4 together with the solutions provided in Sects. 2 and 3, develop a theoretical system, simple enough to be suitable at college level to describe chemical equilibrium and complementary to our previous work [15–17]. It can be seen that this

theoretical approach is developed differently from that suggested by simple logical analysis in elementary chemistry. Section 4 is mainly concerned with the ideal gas system at constant temperature  $T$  and pressure  $P$  but can be extended to more general conditions. The system uses mathematics rather than thermodynamics and can be generally valid in problems where Le Chatelier's principle is not applicable. The difficulties in understanding chemical equilibrium can thus be minimized since more mathematical tools are offered.

In this work it is shown not only that numerical evaluation is a very helpful tool in chemistry presentation, but also that a thorough theoretical investigation via mathematics is necessary in understanding chemistry as is true for any other science subjects [18–21]. Economics has benefited considerably by introducing mathematical approaches demonstrated from the Nobel laureates Maskin, Diamond, Roth and Shapley [22]. In the same way understanding of chemical equilibrium can be increased greatly when a mathematical approach is introduced [10,23]. We have noticed the belief that theories are artificial [24] and in evolution [25] and therefore that rote learning is preferable in which remembering experimental results is sometimes better than meaningful learning [24,26]. However, the implication of this work is to advocate introducing more mathematics within chemical contents and to enhance chemical logic in chemistry. The influence of mathematics on chemistry has grown over the years. However the relationship between chemistry and mathematics is not stressed in elementary chemistry as much as it should be. A significant minority of chemists reject theoretical and mathematical treatments considering that concept understanding is preferable and thereby they can avoid any level of mathematics. Elementary chemistry is still mainly presented in a traditional way where chemistry is presented taxonomically. Although some chemists continue to consider chemistry as a subject that needs to be grasped by rote learning, it has been noticed by many that such a philosophy causes serious educational problems. The oversimplified presentations in introductory courses usually cause misunderstandings that need to be corrected at a later time involving considerable effort [14]. This situation needs to be changed [27,28]. Chemical concepts developed by mathematics can only be understood by mathematical presentation. Elementary chemistry can be presented with more rigor and more logic. In this work it is shown that there are examples where real understanding can only be achieved through mathematical analysis and that conceptual understanding without mathematics often proves superficial.

## 2 Limitations of Le Chatelier's principle demonstrated by changes in conjugated variables

Le Chatelier's principle is usually interpreted as meaning that an equilibrium will be displaced to counteract influence applied from outside. However, this statement is vague and ambiguous [6,29] since the word counteract can refer to the action or the effect caused by that action. For that reason the principle might be more precisely expressed as the following: that an equilibrium would shift to always counteract the action; or alternatively to always counteract the effect caused by that action. But both statements cannot be true and these precise statements do not remove the ambiguity

as is demonstrated below [16]. Subsequently we will present a general mathematical treatment of equilibrium systems in Sect. 4.

A system can be described with pairs of conjugated variables such as temperature  $T$  and the amount of heat absorbed  $q$ ; or pressure  $P$  and volume  $V$ . If no equilibrium exists, then when applying an action such as changing  $T$  or  $P$ , there will be an effect of the action, i.e. a corresponding change in the conjugated variables  $q$  or  $V$ . Conversely, changes in the variables  $q$  or  $V$  will lead to changes in  $T$  or  $P$ .

If there is a chemical equilibrium (e.g. as represented by Eq. 1) which exists in a system, then if decreasing  $P$  or increasing  $T$  is taken as an action, the equilibrium will shift to counteract this action, and counteract the change in  $P$  or  $T$  by a displacement to the side of the chemical equation with a larger sum of coefficients or in the direction of absorbing heat. Thus, in this case the equilibrium is indeed shifted to reduce the action, i.e. to reduce the decrease in  $P$  or increase in  $T$ , conforming to the statement of Le Chatelier's principle that an equilibrium shift always counteracts the action. On the other hand, the effect of decreasing  $P$  or increasing  $T$  is to increase  $V$  or the absorbed heat  $q$ . The equilibrium shifted to the side with a larger sum of coefficients enhances the effect of increasing  $V$  while the equilibrium shifted in the direction of absorbing heat increases the heat  $q$  absorbed by the system, and therefore both shifts will contradict the statement of Le Chatelier's principle that an equilibrium shift always counteracts the effect caused by that action.

On the other hand, if we take an increase in  $V$  or  $q$  as the action and the corresponding decrease in  $P$  or increase in  $T$  as the effect of the corresponding action, then the equilibrium will shift to counteract the effect but enhance the action, thus contradicting Le Chatelier's principle that an equilibrium shift always counteracts the action. The validity of the above discussion can also be demonstrated by using phase equilibria [6, 16] instead of chemical equilibria [8].

By a mathematical [15, 17] or a thermodynamical [8] treatment, a universal law (Theorem 3 in [15]) can be postulated to replace Le Chatelier's principle which accounts for the above mentioned facts i.e. that the equilibrium is shifted to reduce the change in intensive variable while enhancing the change in extensive variable when these are a pair of conjugated variables [8]. It can be noted that the philosophy in this new law from mathematics is quite different from that expressed in the traditional statement of Le Chatelier's principle. This mathematical result can be easily verified using the above mentioned examples and will be analyzed mathematically in the last part of this paper according to previous work [15–17] which is somewhat different from that presented in Ref. [8]. The results from the above discussions which are not compatible with the traditional statement of Le Chatelier's principle are summarized in Table 1. It can be seen from this table that the rigorous mathematical law involving intensive and extensive variables remains valid under all circumstances.

### 3 Limitations of the Le Chatelier's principle demonstrated by numerical calculations

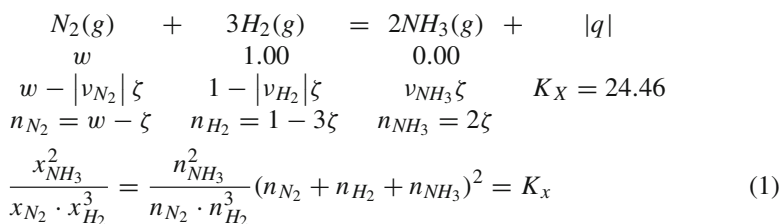
The above example is not the only case in which the logic of Le Chatelier's principle proves to be problematic. Most chemists still think that the equilibrium will be

**Table 1** The equilibrium shift for chemical or phase equilibrium with respect to changes in P and V, or T and q

No.	Action	Effect	Statement of Le Chatelier's principle	Theorem 3
1	P or T	V or q	Counteracts action ✓	Counteracts change in intensive variable ✓
			Counteracts effect ×	Enhances change in extensive variable ✓
2	V or q	P or T	Counteracts action ×	Counteracts change in intensive variable ✓
			Counteracts effect ✓	Enhances change in extensive variable ✓

✓ and × signify whether Le Chatelier's principle or Theorem 3 is consistent or not with the experimental data

displaced to reduce the added species in all situations and as a result when planning experiments often trying by test to add a cheaper reactant in order to increase the conversion ratio of the more expensive reactants [9]. This is in fact only applicable for reactions involving liquids where the volume of the system can be considered as constant and it is not true for more complicated cases involving gaseous systems at constant T and P. This section shows that numerical calculations are helpful in chemistry presentations. It can be shown from Eq. 1 that equilibrium can be shifted to produce more of the added species and reduce the conversion ratio of other reactants. Suppose  $K_x$ , an equilibrium constant expressed in mole fractions, is 24.46 at a certain temperature and pressure for the Haber reaction given in Eq. 1, row 1, with initial conditions, given in row 2, of 1 mole of  $H_2$ ,  $w$  moles of  $N_2$  and none of the product  $NH_3$ . When the reaction progresses with the reaction extent  $\zeta$ , then row 3 or row 4 is obtained where  $\nu$  is the coefficient. It is an exothermal reaction indicated by  $|q|$  in row 1. Row 5 is the equilibrium condition expressed with  $K_x$  and its corresponding reaction quotient  $Q_x$ . Results from calculations with  $w = 1$  and 2 in Eq. 1 are listed in Table 2. All symbols used in this paper are listed in "Appendix 4".



The reaction extent  $\zeta$  at equilibrium can be calculated from Eq. 1. The calculations can be accomplished by the bisection method where  $\zeta$  takes a trying value from 0 to 1/3 [16]. Row No. 1 in Table 2 shows the calculated results for equilibrium when  $w$  is 1 mole. Row No. 2 characterizes the state when 1 more mole of  $N_2$  is added into this equilibrium if the reaction were frozen. The results from the new equilibrium

**Table 2** Calculations with Eq. 1 for  $w = 1$  and 2

No.	w	$\zeta$	$n_{N_2}$	$n_{H_2}$	$n_{NH_3}$	$n_T$	$x_{N_2}$	$x_{H_2}$	$x_{NH_3}$
1	1	0.2330	0.7670	0.3009	0.4661	1.5340	0.5000	0.1962	0.3038
2	2	0.2330	1.7670	0.3009	0.4661	2.5340	0.6973	0.1182	0.1839
3	2	0.2284	1.7716	0.3147	0.4569	2.5432	0.6966	0.1237	0.1797

The data in rows of No. 1 and 3 are equilibrium values calculated for  $w = 1$  and 2, respectively; row of No. 2 gives the result when 1 more mole of  $N_2$  is added in the equilibrium system represented by row of No. 1 while the reaction is frozen at  $\zeta = 0.2330$

for  $w = 2$  are shown by row No. 3. As can be seen by comparing rows No. 2 and No. 3 in Table 2, the added  $N_2$  does not move the new equilibrium forward, but moves it backward to produce more added species as the reaction extent is reduced ( $\zeta_3 - \zeta_2 = 0.2284 - 0.2330 < 0$ ) and both  $n_{N_2}$  and  $n_{H_2}$  are increased and  $n_{NH_3}$  is decreased (rows No. 2 and No. 3), i.e. as  $N_2$  is added, the conversion ratio of  $H_2$  is decreased and more  $N_2$  is produced by the equilibrium shift. Thus, the logic of the traditional statement of Le Chatelier's principle is not always correct.

By the analysis given above, it can be concluded that Le Chatelier's principle cannot be applied in the example represented by Eq. 1, since the concentrations for both  $N_2$  and  $H_2$  are affected by the addition [5]. When 1 mole of  $N_2$  is added  $x_{N_2}$  is increased by 0.5–0.6973 from rows No. 1 to 2 of Table 2, requiring a forward reaction to reduce  $x_{N_2}$ ,<sup>1</sup> but that rise could not be taken in isolation as  $x_{H_2}$  is reduced by 0.1962–0.1182 from rows No. 1 to 2, requiring a backward reaction.<sup>2</sup> The latter were dominant since the coefficient for  $N_2$  in Eq. 1 is 1 and for  $H_2$  is 3.<sup>3</sup> Even this “conceptual understanding” cannot be achieved without arithmetical analysis. However this simple reasoning is not helpful in developing a more general theoretical approach since the increase in total number of moles  $n_T$  by the addition affects the mole fractions for all species but not  $x_{H_2}$  alone.

As can be seen from Table 2 the concentration of  $N_2$  with  $x_{N_2}$  increases by 0.5–0.6973 from row No. 1 to 2 in Table 2 when 1 mole of  $N_2$  is added. The equilibrium shift decreases this increase and initiates a change by 0.6973 to 0.6966 from row No. 2 to 3, consistent with Theorem 3 in [15] while shows a backward reaction can reduce the concentration of  $N_2$  as pointed out in the footnote. However, the final equilibrium concentration increased from the old equilibrium concentration by 0.5 to 0.6966 from row No. 1 to 3, consistent with Theorem 4 in [15] which states that the new equilibrium concentration cannot be lower than the previous one for the added species. This concept in Theorem 4 can only be taught vaguely without mathematical analysis.

The concentration of  $NH_3$   $x_{NH_3}$  decreases by 0.3038 to 0.1839 from row No. 1 to 2 in Table 2 when 1 mole of  $N_2$  is added. However, as can be seen from row No. 3 of

<sup>1</sup> This argument was adopted by those who defend Le Chatelier's principle but it is incomplete since in the actual reaction of Eq. 1 a backward reaction can also reduce the concentration of  $N_2$  by increasing  $n_T$ .

<sup>2</sup> Indeed in such reactions, it is impossible for only one mole fraction to change.

<sup>3</sup> But without a detailed mathematical analysis, it cannot explain why this effect is not dominant when  $w < 1$ . A forward reaction instead of a backward reaction will be initiated by adding  $N_2$  if  $w < 1$  in Eq. 1.

the Table 2 the equilibrium shifts further to change the concentration to 0.1797, thus a decrease rather than an increase. The result contradicts with Le Chatelier's principle but does not contradict with Theorem 3 since Theorem 3 refers to conjugated variables.  $x_{N_2}$  and the number of moles of  $N_2$ ,  $n_{N_2}$ , are conjugated variables but  $x_{NH_3}$  and  $n_{N_2}$  are not. Conjugated variables are discussed further in "Appendix 3".

## 4 A theoretical solution to the dilemma of Le Chatelier's principle

### 4.1 Background information

The numerical calculations in the above section show the problems with the applications of Le Chatelier's principle. Solving a problem numerically does not necessarily mean understanding the chemistry. It is not sufficient in scientific analysis to demonstrate theories only with specific examples involving numerical calculations. It is more useful to obtain a general understanding with theoretical analysis. A simple analysis [5] shows that the addition of  $N_2$  at constant T and P will produce more  $N_2$  because of the dilution of  $H_2$  resulting from the addition. But it will be clear that this explanation does not help much in developing a more systematic mathematical method [15–17].

The added  $j$  increases both  $n_j$  and  $n_T$  by  $dn_j$  in  $x_j = n_j/n_T$  and in the denominator of  $x_i = n_i/n_T$  of the expression of  $Q_x$  in Eq. 3. It should be noted that the change in  $n_j$  only affects  $x_j$  but the change in  $n_T$  affects  $x_i$  for all  $i$ . The effects on  $Q_x$  of both the changes in  $n_j$  and  $n_T$  need to be considered in a more rigorous and general analysis. Rigorous and general understanding are the real aims for a higher level of pedagogy and the goal of scientific research. In order to achieve this aim, it is necessary to start with the general equation for chemical equilibrium

$$0 = \sum_{i=1}^N v_i A_i \quad (2)$$

where  $A_i$  represents the chemical species present in the system.  $v_i$  is the coefficient of species  $A_i$  in the balanced reaction and is positive for product and negative for reactant. Note that when referring to a reactant,  $i=r$ ; and to a product  $i=p$ . Equation 2 conforms to this convention.  $N$  is the total number of species in the reacting system. The equal sign is obligatory to balance the numbers of each element contained in reactant and product. A general form of the reaction quotient  $Q_x$  with respect to the mole fraction  $x_i$  with species  $A_i$  in Eq. 2 is defined as Eq. 3.

$$Q_x = \prod_{i=1}^N x_i^{v_i} = \frac{\prod_{i=1}^N n_i^{v_i}}{n_T^{\Delta v}} = n_T^{-\Delta v} \prod_{i=1}^N n_i^{v_i} \quad (3)$$

where  $n_i$  is the number of moles of species  $A_i$  and  $n_i^0$  is its initial value.  $n_T$  is the total number of moles in the system.  $\Delta v$  is the sum of all the coefficients  $v_i$  in the chemical equation. Although  $Q_x$  is not directly related to T and P from Eq. 3, it can be

shown from thermodynamics that the equilibrium value of  $Q_x$  for an ideal gas system at constant T and P is a constant and it is indicated by  $K_x$ . When the reaction quotient is expressed in partial pressures,  $Q_p$  is used and the corresponding equilibrium constant is  $K_p$ . It can be shown that [15]

$$\begin{aligned} \frac{n_T}{Q_x} \left( \frac{\partial Q_x}{\partial \zeta} \right)_{n_i} &= \frac{n_T}{Q_x} \left( \frac{\partial Q_x}{\partial \zeta} \right)_{n_i^0} = n_T \left[ \left( \sum_{i=1}^N \frac{v_i^2}{n_i} \right) - \frac{(\Delta v)^2}{n_T} \right] \\ &= \left[ n_T \left( \sum_{i=1}^N \frac{v_i^2}{n_i} \right) - \left( \sum_{i=1}^N v_i \right)^2 \right] \end{aligned} \quad (4)$$

It can be proved [15] that

$$\left( \frac{\partial Q_x}{\partial \zeta} \right)_{n_i} \geq 0 \quad (5)$$

In chemistry Eq. 2 is usually written as Eq. 6.

$$\sum_{i=1}^{N_r} |v_{r_i}| A_{r_i} = \sum_{i=1}^{N_p} v_{p_i} A_{p_i} \quad (6)$$

where r indicates reactant and p product;  $N_r$  and  $N_p$  are the total number of reactants and products, respectively. The meaning within the mathematical inequality Eq. 5 [15] is that the forward reaction will increase  $Q_x$  and the backward reaction decrease it, i.e. that  $\left( \frac{\partial Q_x}{\partial \zeta} \right)_{n_i} > 0$  is the general formula fitting a majority of problems. It is true that under special conditions  $Q_x$  is unchanged by the forward or backward reaction and thus  $\left( \frac{\partial Q_x}{\partial \zeta} \right)_{n_i} = 0$  but this situation is very rare since from Eq. 15 it can be shown that it only occurs when all the initial moles of the gaseous species are in the same proportion as their coefficients in the chemical reaction and also that there are gaseous species only on one side of the equation while on the other side there are solid or liquid species [15].

### Proof of Eq. 5

Equation 4 can be rewritten as

$$\begin{aligned} \left( \frac{\partial Q_x}{\partial \zeta} \right)_{n_i} &= \frac{Q_x}{n_T} \left[ n_T \sum_{i=1}^N \frac{v_i^2}{n_i} - \left( \sum_{i=1}^N v_i \right)^2 \right] \\ &= \frac{Q_x}{n_T} \left[ \left( \sum_{i=1}^N n_i \right) \sum_{i=1}^N \frac{v_i^2}{n_i} - \left( \sum_{i=1}^N v_i \right)^2 \right] \end{aligned} \quad (7)$$



On expanding

$$\begin{aligned}
 \left(\sum_{i=1}^N n_i\right) \sum_{j=1}^N \frac{v_j^2}{n_j} &= v_1^2 + n_1 \frac{v_2^2}{n_2} + n_1 \frac{v_3^2}{n_3} + n_1 \frac{v_4^2}{n_4} + \dots + n_1 \frac{v_N^2}{n_N} \\
 &\quad + n_2 \frac{v_1^2}{n_1} + v_2^2 + n_2 \frac{v_3^2}{n_3} + n_2 \frac{v_4^2}{n_4} + \dots + n_2 \frac{v_N^2}{n_N} \\
 &\quad + n_3 \frac{v_1^2}{n_1} + n_3 \frac{v_2^2}{n_2} + v_3^2 + n_3 \frac{v_4^2}{n_4} + \dots + n_3 \frac{v_N^2}{n_N} \\
 &\quad + n_4 \frac{v_1^2}{n_1} + n_4 \frac{v_2^2}{n_2} + n_4 \frac{v_3^2}{n_3} + v_4^2 + \dots + n_4 \frac{v_N^2}{n_N} \\
 &\quad \dots \\
 &\quad + n_N \frac{v_1^2}{n_1} + n_N \frac{v_2^2}{n_2} + n_N \frac{v_3^2}{n_3} + n_N \frac{v_4^2}{n_4} + \dots + v_N^2 \tag{8}
 \end{aligned}$$

Rearrange the right hand side of Eq. 8 by row

$$\begin{aligned}
 \left(\sum_{i=1}^N n_i\right) \sum_{j=1}^N \frac{v_j^2}{n_j} &= \left(v_1^2 + n_1 \sum_{j>1}^N \frac{v_j^2}{n_j}\right) + \left(n_2 \sum_{j=1}^{j<2} \frac{v_j^2}{n_j} + v_2^2 + n_2 \sum_{j>2}^N \frac{v_j^2}{n_j}\right) \\
 &\quad + \left(n_3 \sum_{j=1}^{j<3} \frac{v_j^2}{n_j} + v_3^2 + n_3 \sum_{j>3}^N \frac{v_j^2}{n_j}\right) \\
 &\quad + \left(n_4 \sum_{j=1}^{j<4} \frac{v_j^2}{n_j} + v_4^2 + n_4 \sum_{j>4}^N \frac{v_j^2}{n_j}\right) + \dots + \left(n_N \sum_{j=1}^{N-1} \frac{v_j^2}{n_j} + v_N^2\right) \\
 &= \sum_{i=2}^N n_i \sum_{j=1}^{j<i} \frac{v_j^2}{n_j} + \sum_{i=1}^N v_i^2 + \sum_{i=1}^{N-1} n_i \sum_{j>i}^N \frac{v_j^2}{n_j} \tag{9}
 \end{aligned}$$

Or by column

$$\begin{aligned}
 \left(\sum_{i=1}^N n_i\right) \sum_{j=1}^N \frac{v_j^2}{n_j} &= \left(\frac{v_1^2}{n_1} \sum_{i>1}^N n_i + v_1^2\right) + \left(\frac{v_2^2}{n_2} \sum_{i>2}^N n_i + v_2^2 + \frac{v_2^2}{n_2} \sum_{i=1}^{i<2} n_i\right) \\
 &\quad + \left(\frac{v_3^2}{n_3} \sum_{i>3}^N n_i + v_3^2 + \frac{v_3^2}{n_3} \sum_{i=1}^{i<3} n_i\right) \\
 &\quad + \left(\frac{v_4^2}{n_4} \sum_{i>4}^N n_i + v_4^2 + \frac{v_4^2}{n_4} \sum_{i=1}^{i<4} n_i\right) + \dots + \left(v_N^2 + \frac{v_N^2}{n_N} \sum_{j=1}^{N-1} n_j\right) \\
 &= \sum_{j=1}^{N-1} \frac{v_j^2}{n_j} \sum_{i>j}^N n_i + \sum_{i=1}^N v_i^2 + \sum_{j=2}^N \frac{v_j^2}{n_j} \sum_{i=1}^{i<j} n_i \tag{10}
 \end{aligned}$$

Since

$$\sum_{i=2}^N n_i \sum_{j=1}^{j<i} \frac{v_j^2}{n_j} = \sum_{j=1}^{N-1} \frac{v_j^2}{n_j} \sum_{i>j}^N n_i \quad (11)$$

$$\sum_{i=1}^{N-1} n_i \sum_{j>i}^N \frac{v_j^2}{n_j} = \sum_{j=2}^N \frac{v_j^2}{n_j} \sum_{i=1}^{i<j} n_i \quad (12)$$

Equation 11 accounts for the lower triangle in Fig. 1 and Eq. 12 accounts for the upper triangle. With Eqs. 11 and 12, we obtain

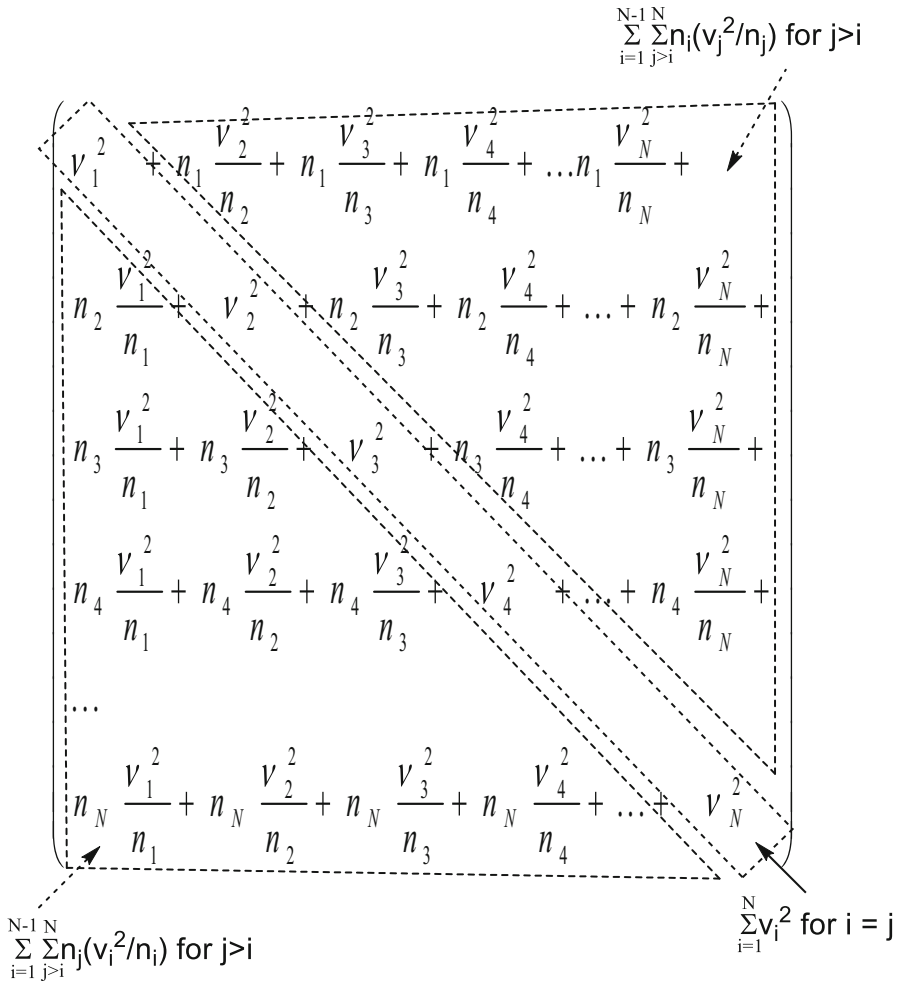
$$\begin{aligned} \left( \sum_{i=1}^N n_i \right) \sum_{j=1}^N \frac{v_j^2}{n_j} &= \sum_{i=2}^N n_i \sum_{j=1}^{j<i} \frac{v_j^2}{n_j} + \sum_{i=1}^N v_i^2 + \sum_{i=1}^{N-1} n_i \sum_{j>i}^N \frac{v_j^2}{n_j} \\ &= \sum_{j=1}^{N-1} \frac{v_j^2}{n_j} \sum_{i>j}^N n_i + \sum_{i=1}^N v_i^2 + \sum_{i=1}^{N-1} n_i \sum_{j>i}^N \frac{v_j^2}{n_j} \\ &= \sum_{i=1}^N v_i^2 + \sum_{j=1}^{N-1} \sum_{i>j}^N n_i \frac{v_j^2}{n_j} + \sum_{i=1}^{N-1} \sum_{j>i}^N n_i \frac{v_j^2}{n_j} \\ &= \sum_{i=1}^N v_i^2 + \sum_{i=1}^{N-1} \sum_{j>i}^N n_j \frac{v_i^2}{n_i} + \sum_{i=1}^N \sum_{j>i}^N n_i \frac{v_j^2}{n_j} \\ &= \sum_{i=1}^N v_i^2 + \sum_{i=1}^{N-1} \sum_{j>i}^N \frac{n_j^2 v_i^2 + n_i^2 v_j^2}{n_i n_j} \end{aligned} \quad (13)$$

$$\left( \sum_{i=1}^N v_i \right)^2 = \sum_{i=1}^N v_i^2 + 2 \sum_{i=1}^{N-1} \sum_{j>i}^N v_i v_j \quad (14)$$

Inserting Eqs. 13 and 14 into Eq. 7 we obtain Eq. 15.

$$\begin{aligned} \left( \frac{\partial Q_x}{\partial \zeta} \right)_{n_i} &= \frac{Q_x}{n_T} \left[ \left( \sum_{i=1}^N n_i \right) \sum_{i=1}^N \frac{v_i^2}{n_i} - \left( \sum_{i=1}^N v_i \right)^2 \right] \\ &= \frac{Q_x}{n_T} \sum_{i=1}^N \sum_{j>i}^N \frac{(n_i v_j - n_j v_i)^2}{n_i n_j} \geq 0 \end{aligned} \quad (15)$$

Equation 5 is an important result in chemical equilibrium and it signifies that the forward reaction will increase  $Q_x$  and the backward reaction decrease it. The main ideas in the proof are summarized in Fig. 1 and Theorem 1 [15] is obtained from



**Fig. 1** An outline showing the main principles within the proof of Eq. 5. Equation 11 is represented by the lower triangle and Eq. 12 by the upper

Eq. 5. If  $i = r_i$  and  $j = p_j$  there will be non-zero terms with  $(n_{r_i} v_{p_j} - n_{p_j} v_{r_i})^2 = (n_{r_i} v_{p_j} + n_{p_j} |v_{r_i}|)^2 > 0$  in Eq. 15 which is exactly characterized by Theorem 1 since there are gaseous species on both sides of the chemical equation [15]. Still another Proof of Theorem 1 with gaseous species on both sides of the chemical equation is given in “Appendix 1”.

This represents a significant difference between mathematical chemistry and pure mathematics. Equation 15 is mathematically wrong but chemically correct since either  $Q_x$  or  $n_i$  can be negative in mathematics which allows  $(\frac{\partial Q_x}{\partial \xi})_{n_i}$  to be less than zero while in chemistry both  $Q_x$  and  $n_i$  must both be positive. If the initial mole numbers of all products are zero, then Eq. 15' can be proved from Eq. 15 [15].

$$\begin{aligned}
\frac{n_T}{Q_x} \left( \frac{\partial Q_x}{\partial \zeta} \right)_{n_i} &= \sum_r \sum_{r' > r} \frac{(v_r n_{r'}^0 - v_{r'} n_r^0)^2}{n_r n_{r'}} + \sum_r \sum_p \frac{(n_r^0)^2 v_p^2}{n_r n_p} + \sum_i \sum_l \frac{n_i v_l^2}{n_l} \\
&= \sum_r \sum_{r' > r} \frac{(v_r n_{r'}^0 - v_{r'} n_r^0)^2}{n_r n_{r'}} + \sum_p v_p \left( \sum_r \frac{n_r^0 - v_r \zeta}{\zeta} + \zeta \sum_r \frac{v_r^2}{n_r} \right) \\
&\quad + \sum_i \sum_l \frac{n_i v_l^2}{n_l} \geq 0
\end{aligned} \tag{15'}$$

In Eq. 15',  $i$  is the inert species while  $l$  is a general index for any species. Theorem 1 in Ref. [15] is restated in the following section with some modifications assimilating the discussed points discussed there.

**Theorem 1** (a)  $Q_x$  cannot be changed in a reaction if the ratio of the initial number of moles of all the species is equal to the ratio of the coefficients of all those species. (b) Otherwise, the forward reaction will increase  $Q_x$  and the backward reaction will decrease  $Q_x$ .  $Q_x$  is the reaction quotient expressed in mole fractions.

**Corollary i**  $Q_x$  does not change when a reaction is proceeded forward or backward only when the equation  $\frac{n_k^0}{n_i^0} = \frac{v_k}{v_i}$  is valid for all species presented in the equilibrium.

**Corollary ii** (a) cannot occur when there are gaseous species on both sides of the chemical equation.

**Corollary iii** (a) cannot occur when there are inert gaseous species present.

The other aspects of Theorem 1 have been detailed in previous work [15, 16]. A mathematical Proof for Theorem 1 is necessary since it cannot be obtained intuitively because the changes in the numerator and the denominator of  $Q_x$  in Eq. 3 caused by the equilibrium shift will always change  $Q_x$  in opposite directions independent of whether  $\Delta v > 0$  or  $\Delta v < 0$ , or whether the shift refers to a forward or backward reaction. For example, a forward reaction increases  $n_p$  and decreases  $n_r$  thus  $\prod_{i=1}^N n_i^{v_i}$  is increased (Eq. 3). The forward reaction also increases  $n_T^{\Delta v}$ , the denominator of  $Q_x$  if  $\Delta v > 0$ , i.e.  $n_T$  is increased as is the denominator of  $Q_x$  which makes  $Q_x$  decrease. If  $\Delta v < 0$  the forward reaction decreases  $n_T$  but still increases the denominator  $n_T^{\Delta v}$  in Eq. 3 and therefore decreases  $Q_x$ . Thus the forward reaction increases both the numerator and denominator of  $Q_x$  under any conditions and these increases will have opposite effects on  $Q_x$  and therefore it is impossible to establish intuitively which effect is dominant. This conclusion is also valid for the backward reaction. These two opposite effects discussed above are also reflected on the right side of Eq. 7 by the positive and negative terms. This discussion concerning the numerator and denominator of  $Q_x$  is also useful as shown below for Theorem 2.

Only with mathematics can it be made clear that the effect on the numerator represented in Eq. 7 is dominant. Using Theorem 1 it is possible to cover all the parts

of equilibrium theory that are usually found in current curricula. At equilibrium  $Q_x$  is equal to the equilibrium constant  $K_x$ . When the temperature  $T$  is increased, then  $K_x$  will increase for an endothermic reaction and decrease for an exothermic reaction. According to Theorem 1, the equilibrium shifts to the right for an endothermic reaction and to the left for an exothermic reaction.  $Q_p$  is equal to the equilibrium constant  $K_p$  for a gaseous equilibrium at constant  $T$ . When the chemical reaction in an equilibrium system is frozen, an increase in pressure  $P$  will increase  $Q_p$  if  $\Delta v > 0$  or decrease  $Q_p$  if  $\Delta v < 0$  since  $Q_p = Q_x P^{\Delta v}$ . Thus, Theorem 1 ensures that an increase in the total pressure will shift the equilibrium to the side of the chemical reaction with a smaller sum of coefficients in order to change  $Q_x$  to properly adjust the value of  $Q_p$ . Alternatively,  $K_p = K_x P^{\Delta v}$ . When increasing pressure while keeping  $T$  constant,  $K_p$  remains constant while  $K_x$  decreases if  $\Delta v > 0$  or increases if  $\Delta v < 0$ . To reach a new equilibrium, Theorem 1 ensures that a backward reaction will occur to decrease  $Q_x$  to the new  $K_x$  for  $\Delta v > 0$  while a forward reaction will occur to increase  $Q_x$  for  $\Delta v < 0$ . For the phase equilibrium between liquid water and water vapor,  $Q_x = 1$  and  $Q_p = P_{\text{H}_2\text{O}(\text{g})}$ . This represents the special case for Eq. 5 since a change in phase equilibrium does not change  $Q_x$ . However, increasing  $P_{\text{H}_2\text{O}(\text{g})}$  from an equilibrium will cause  $Q_p$  to become greater than  $K_p$  and thus more water vapor will convert to liquid water to reach a new equilibrium. The above discussion essentially covers all the contents in elementary courses concerning equilibrium.

## 4.2 A theoretical analysis of the gaseous equilibrium at constant T and P

With mathematics the general conditions can be derived for an equilibrium shift to produce more of the added species. From Eq. 3 we can also obtain Eq. 16 when the relevant reaction is frozen [15].

$$\begin{aligned} \left( \frac{\partial Q_x}{\partial n_j} \right)_{\zeta, n_i} &= \left( \prod_{i \neq j} n_i^{v_i} \right) v_j n_j^{v_j-1} n_T^{-\Delta v} \frac{n_j}{n_j} + \left( \prod_{i \neq j} n_i^{v_i} \right) n_j^{v_j} (-\Delta v) n_T^{-\Delta v-1} \frac{n_T}{n_T} \\ &= \frac{v_j}{n_j} Q_x - \frac{n_j \Delta v}{n_j n_T} Q_x = Q_x \frac{v_j - x_j \Delta v}{n_j} = \left( \frac{\partial Q_x}{\partial n_j^0} \right)_{\zeta, n_i^0} \end{aligned} \quad (16)$$

$Q_x$ ,  $x_j$ ,  $n_T$  are always greater than zero. For an ideal gaseous system at constant  $T$  and  $P$  for equilibrium,  $Q_x = K_x$ . If a reacting species  $A_j$  in Eq. 2 is added into the equilibrium system,  $Q_x$  will be changed according to Eq. 16 and  $Q_x$  deviates from  $K_x$ . If  $Q_x$  is increased by the addition, i.e.  $\left( \frac{\partial Q_x}{\partial n_j} \right)_{\zeta, n_i} > 0$ , the equilibrium will shift to the left in Eq. 6 to decrease  $Q_x$  according to Eq. 5, the general case of  $\left( \frac{\partial Q_x}{\partial \zeta} \right)_{\zeta, n_i} > 0$  and Theorem 1. If  $Q_x$  is decreased by the addition, i.e.  $\left( \frac{\partial Q_x}{\partial n_j} \right)_{\zeta, n_i} < 0$ , the equilibrium will shift to the right in Eq. 6 to increase  $Q_x$  according to Eq. 5 or Theorem 1.

**Table 3** Equilibrium shifts obtained after adding a species  $j$ 

No	$v_j$	$\Delta v$	$x_j$	$\left(\frac{\partial Q_x}{\partial n_j}\right)_{n_i}$	Equilibrium shift
1	$>0$	$<0$	Any allowed value	$>0$	Backward ✓
2	$>0$	$=0$	Any allowed value	$>0$	Backward ✓
3	$>0$	$>0$	$< \frac{v_j}{\Delta v}$	$>0$	Backward ✓
4	$>0$	$>0$	$> \frac{v_j}{\Delta v}$	$<0$	Forward ×
5	$<0$	$<0$	$< \frac{v_j}{\Delta v}$	$<0$	Forward ✓
6	$<0$	$<0$	$> \frac{v_j}{\Delta v}$	$>0$	Backward ×
7	$<0$	$=0$	Any allowed value	$<0$	Forward ✓
8	$<0$	$>0$	Any allowed value	$<0$	Forward ✓

✓ and × signify whether the traditional statement of Le Chatelier's principle is true or false

If the product  $A_j$  ( $v_j > 0$ ) is added to the equilibrium,  $Q_x$  increases when  $\Delta v = 0$  or  $\Delta v < 0$  since  $\left(\frac{\partial Q_x}{\partial n_j}\right)_{\zeta, n_i} > 0$  from Eq. 16 when  $A_j$  is a product where  $v_j > 0$ . Thus the addition of product  $A_j$  will make  $Q_x > K_x$  if the reaction is frozen. In order to restore the equilibrium,  $Q_x$  must decrease to  $K_x$ . According to Eq. 5 or Theorem 1 the equilibrium will shift to the left in Eq. 6 to decrease  $Q_x$ . i.e. The addition of the product  $A_j$  will shift the equilibrium to reduce the added product  $A_j$ . When the product  $A_j$  is on the side of Eq. 6 with the larger sum of the coefficients ( $\Delta v > 0$ ), there will be two different possibilities.  $\left(\frac{\partial Q_x}{\partial n_j}\right)_{\zeta, n_i} > 0$  is still maintained according to Eq. 16 when  $x_j < \frac{v_j}{\Delta v}$  which means that the addition of a product will shift the equilibrium to the reactant side to reduce the added product. However,  $\left(\frac{\partial Q_x}{\partial n_j}\right)_{\zeta, n_i} < 0$  when  $x_j > \frac{v_j}{\Delta v}$  which means that the addition of product  $A_j$  will shift the equilibrium to increase the added  $A_j$ , contradicting Le Chatelier's principle. On the other hand, if the added species  $A_j$  is a reactant ( $v_j < 0$ ), then  $Q_x$  decreases when  $\Delta v \geq 0$  since  $\left(\frac{\partial Q_x}{\partial n_j}\right)_{\zeta, n_i} < 0$  from Eq. 16 where  $v_j < 0$  and  $\Delta v \geq 0$ . Thus the addition of reactant  $A_j$  will make  $Q_x < K_x$  if the reaction is frozen. In order to increase  $Q_x$  the equilibrium will shift to the right in Eq. 6 according to Eq. 5 or Theorem 1, i.e. the addition of the reactant  $A_j$  will shift the equilibrium to reduce the added reactant  $A_j$ . When the reactant side of Eq. 6 has a larger sum of the coefficients ( $\Delta v < 0$ ), there will also be two different possibilities. The inequality  $\left(\frac{\partial Q_x}{\partial n_j}\right)_{\zeta, n_i} < 0$  is still held when  $x_j < \frac{v_j}{\Delta v}$  which means that the addition of a reactant will shift the equilibrium to the side that reduces the amount of added reactant. However,  $\left(\frac{\partial Q_x}{\partial n_j}\right)_{\zeta, n_i} > 0$  when  $x_j > \frac{v_j}{\Delta v}$  which means that the addition of  $A_j$  will shift the equilibrium to increase the added  $A_j$ , also contradicting Le Chatelier's principle. The results are summarized in Table 3.

As can be seen in Table 3, the equilibrium will be displaced to produce more of the added species at rows 4 and 6 thus contradicting Le Chatelier's principle while all the other rows indicate that the equilibrium shifts to reduce the added species, i.e.

$\left(\frac{\partial Q_x}{\partial n_j}\right)_{\zeta, n_i}$  must be negative if the equilibrium is required to be displaced to produce more added product ( $v_j > 0$ ). This is shown in row 4 where  $\Delta v > 0$  and  $x_j > \frac{v_j}{\Delta v}$  are the required conditions. Note that both  $v_j$  and  $\Delta v$  are positive. On the other hand,  $\left(\frac{\partial Q_x}{\partial n_j}\right)_{\zeta, n_i}$  must be positive if the equilibrium is required to be displaced to produce more added reactant ( $v_j < 0$ ). This is shown in row 6 where  $\Delta v < 0$  and  $x_j > \frac{v_j}{\Delta v}$ . Note that in this case, both  $v_j$  and  $\Delta v$  are negative. The common features necessary for the equilibrium to shift to produce more of the added species, either a product or a reactant, are  $x_j > \frac{v_j}{\Delta v}$  and  $\frac{v_j}{\Delta v} > 0$ .  $\frac{v_j}{\Delta v} > 0$  means that the added species is on the side of the chemical equation with the greater sum of coefficients. Since  $x_j$  is positive, it is only if  $\frac{v_j}{\Delta v} > 0$  that the condition  $x_j > \frac{v_j}{\Delta v}$  can be satisfied.

In Eq. 1,  $N_2$  is on the side with the larger sum of coefficients in the balanced chemical equation and the equilibrium mole fraction of  $N_2$  calculated when  $w = 1$  satisfies  $x_{N_2} = \frac{v_{N_2}}{\Delta v} = \frac{-1}{-2} = 0.5$ , thus the subsequent addition of more  $N_2$  will result in an equilibrium shift increasing the production of  $N_2$ . The equilibrium mole fractions will satisfy  $x_{H_2} = \frac{n_{H_2}}{n_T} = \frac{v_{H_2}}{\Delta v} = \frac{-3}{-2} > 1$  if more  $H_2$  is produced by adding more  $H_2$  to the equilibrium system. But this condition can never be achieved since  $x_{H_2}$  is always less than 1. Without the detailed mathematics, the general condition for producing more added species discussed here cannot be derived and therefore the result cannot be readily understood.

It is recognized [5] that the equilibrium shift to produce more of the added  $N_2$  in Eq. 1 occurs because  $H_2$  is diluted by the addition. It has been argued that Le Chatelier's principle is only applicable to system where the change involves only a single variable and not to systems, like the Haber process described in Eq. 1 when both the concentrations of  $N_2$  and  $H_2$  are changed by an addition. As can be seen the conclusion from such simple analysis is not helpful in developing the deep mathematical treatment explained in this work. What is more, as shown from Table 1, Le Chatelier's principle is not applicable even in cases where only a pair of variables, T and q or P and V, are involved. The partial derivative used in the mathematical approach considers only a pair of variables where all the other variables are kept as constants. However, it is possible by using calculus to assemble all the partial derivatives to give a complete view of the system which cannot be achieved using Le Chatelier's principle. Thus the rigorous mathematical approach deserves a place in modern chemistry while following Chang [5], it is correct to state that Le Chatelier's principle does not.

In Eq. 3 if we define the numerator  $N_x$  as

$$N_x = \prod_{i=1}^N n_i^{v_i} \quad (17)$$

and the denominator as

$$D_x = n_T^{\Delta v} \quad (18)$$

It can be shown that the results discussed above can also be obtained by application of Theorem 2 obtained mathematically [15, 16] for a gaseous equilibrium at constant

T and P. Corollary v is a natural result of Theorem 1. Some mathematical aspects for Theorem 2 are presented in “Appendix 2”.

**Theorem 2** When adding a species  $j$  into a gas equilibrium system at constant  $T$  and  $P$ , (a) the change in total number of moles  $n_T$  caused by the addition would shift the equilibrium to the side of the chemical equation for which the sum of coefficients is the greater; (b) the change in the number of moles,  $n_j$ , for species  $j$  caused by the addition would shift the equilibrium to the side of reducing the amount of that species.

**Corollary i to (a)** On diluting an equilibrium system by adding an inert species, the equilibrium will shift to the side of the chemical equation with the greater sum of coefficients.

**Corollary ii** Effects (a) and (b) are synergistic if  $\frac{v_j}{\sum_i v_i} = \frac{v_j}{\Delta v} < 0$  but opposite if  $\frac{v_j}{\Delta v} > 0$ . (a) is dominant and overrides (b) only if  $x_j > \frac{v_j}{\Delta v}$  or  $\frac{n_j^0}{\sum_{i \neq j} n_i^0} > \frac{v_j}{\sum_{i \neq j} v_i}$ .

**Corollary iii** Both the total amount of moles in a system  $n_T$  and the mole number for  $j$ ,  $n_j$ , will be increased when species  $j$  is added into a system. The increase in  $n_T$  (a) and in  $n_j$  (b) will each have the effect of changing  $Q_x$ . Corollary ii applies to these two effects for both (a) and (b).

**Corollary iv** Both  $n_T$  and  $n_k$  will be changed when the reaction goes forward or backward. The change in (a)  $n_T$  and in (b)  $n_k$  will each change the mole fraction of  $k$ . Corollary ii applies to these two effects for both (a) and (b).

**Corollary v** Both  $n_T$  and  $n_i$  of each species  $i$  will be changed when the reaction goes forward or backward. (b) the effects on  $Q_x$  of all changes in  $n_i$  caused by the change of reaction extent is synergistic but opposite to (a), the effect on  $Q_x$  of change  $n_T$  caused by the same reaction extent change. The summed effect from (b) will always override that from (a).

**Corollary vi**  $\frac{v_j}{\Delta v} < 0$  signifies that species  $j$  is on the side of the reaction equation with smaller sum of coefficients while  $\frac{v_j}{\Delta v} > 0$  signifies that species  $j$  is on the side of the reaction equation with larger sum.

**Corollary vii**  $x_j \geq \frac{v_j}{\Delta v}$  is valid only if  $\frac{v_j}{\Delta v} > 0$  is true.  $\frac{n_j^0}{\sum_{i \neq j} n_i^0} > \frac{v_j}{\sum_{i \neq j} v_i}$  is valid only if  $\frac{v_j}{\sum_{i \neq j} v_i} > 0$ .

If a product  $j$  ( $v_j > 0$ ) is added in a gaseous equilibrium at constant  $T$  and  $P$  and if the product side in the chemical equation has a smaller sum of coefficients ( $\Delta v < 0$ ), then the change in  $n_T$  initiates a backward reaction (Theorem 2a) to reduce the amount of  $j$  as does the change in  $n_j$  (Theorem 2b). Here  $\frac{v_j}{\Delta v} < 0$  since  $v_j > 0$  and  $\Delta v < 0$  and as stipulated in Corollary ii of Theorem 2 the equilibrium displaces the reaction in the same direction by the two effects. If the product side has a larger sum of coefficients  $\Delta v > 0$ , then Theorems 2a and 2b will initiate opposite displacements as stated in corollary ii since  $\frac{v_j}{\Delta v} > 0$  because  $v_j > 0$  and  $\Delta v > 0$ . As stated in Corollary ii, 2b



is dominant if  $x_j < \frac{v_j}{\Delta v}$  and thus the equilibrium shifts to reduce the added species  $j$  while 2a is dominant if  $x_j > \frac{v_j}{\Delta v}$  and the equilibrium shifts to increase  $j$ . The same analysis applies when the added species is a reactant. Theorem 2 thus gives the same results discussed above. The conclusions in Theorem 2 can be generalized to apply in the examples given below.

For ideal gases,  $n_T$  is related to the volume  $V$  of the system.

$$n_T = kV; \quad \text{where } k = \frac{P}{RT} \quad (19)$$

Using the result from Eq. 19, Eq. 3 becomes

$$Q_x = \frac{\prod_{i=1}^N n_i^{v_i}}{V^{\Delta v}} \left( \frac{P}{RT} \right)^{-\Delta v} = Q_c \left( \frac{P}{RT} \right)^{-\Delta v} \quad (20)$$

where

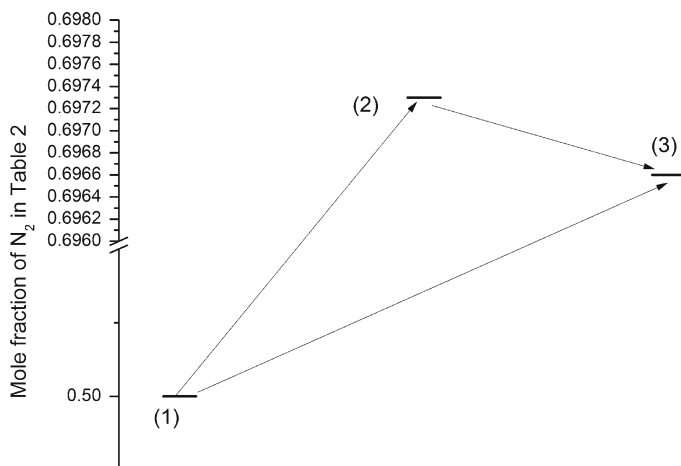
$$Q_c = \frac{\prod_{i=1}^N n_i^{v_i}}{V^{\Delta v}} \quad (21)$$

Now the denominator in Eq. 3 becomes  $V^{\Delta v}$  in Eq. 21 and Theorem 2a becomes corollary i. For example when an inert species is added into a gaseous equilibrium at constant  $T$  and  $P$ , the numerator in Eq. 21 is not affected, thus there is no effect caused by Theorem 2b. But Theorem 2a is still a real effect caused by the increase in the denominator  $V^{\Delta v}$ . Adding inert gases to a chemical equilibrium at constant  $T$  and  $P$ , only the volume of the system is increased by the addition. The equilibrium shift is in fact aggravating the change in volume which is contrary to Le Chatelier's principle.

Thus, even in systems where only one variable is changed with constant  $T$  and  $V$ , the application of Le Chatelier's principle can still be questionable. In fact there is not a universal proof of Le Chatelier's principle even when only a single variable is changed. If an inert species is added into the gaseous equilibrium at constant  $V$ , the variable changed in the system only involves the inert gas which does not participate in the reaction. Even though the total pressure  $P$  and  $n_T$  are affected by this addition, they do not affect the equilibrium itself since the ratio of partial pressures for  $Q_P$  does not change and  $Q_P$  is not affected by the total pressure and  $n_T$  because

$$\begin{aligned} Q_P &= P^{\Delta v} Q_x = P^{\Delta v} n_T^{-\Delta v} \prod_i n_i = P^{\Delta v} \left( \frac{PV}{RT} \right)^{-\Delta v} \prod_i n_i \\ &= \left( \frac{1}{RT} \right)^{-\Delta v} \frac{\prod_i n_i}{(V)^{\Delta v}} = (Q_c RT)^{\Delta v} \end{aligned}$$

$Q_c$  is the reaction quotient in molarities. Thus, adding inert gases does not affect the reaction quotient  $Q_P$ . However, Le Chatelier's principle predicts an equilibrium shift to reduce the total amount of moles  $n_T$  which is wrong since adding inert gases



**Fig. 2** A graphical representation for Eqs. 24, 30, and 31. It shows the relative positions of the mole fraction  $x_{N_2}$  in rows 1, 2 and 3 in Table 2

to a chemical equilibrium at constant T and V cannot initiate an equilibrium shift. For liquid reactions, V in Eq. 21 is constant whatever the value of  $n_T$  if the amount of solvent is not changed, thus only the effect caused by Theorem 2b needs be considered and after adding a reactant or a product the equilibrium will shift to reduce that added species.

### 4.3 Concentration and equilibrium shift

Although the equilibrium is shifted to produce more  $N_2$  from row 2 to row 3 in Table 2, the concentration  $x_{N_2}$  is decreased by the shift but increased with respect to the original equilibrium concentrations shown in row 1 [16]. The concentration changes of  $N_2$  in Eq. 1 shown in Table 2 are represented in Fig. 2.

The result is that the equilibrium is shifted to oppose the change in intensive variable  $x_{N_2}$  but to increase change in its conjugated extensive variable  $n_{N_2}$ . To reach the same increase in  $x_{N_2}$  when a chemical equilibrium exists in the system, more  $N_2$  needs to be added than when no equilibrium exists, which means that the equilibrium enhances the change in extensive variable  $n_{N_2}$  [8, 16, 17].

#### Theoretical explanation

The results shown in Fig. 2 can be justified mathematically with the following Eqs. 24, 30, and 31 [30]. From

$$x_j = x_j(n_j, \zeta) = x_j[n_j, \zeta(n_j, Q_x)] \quad (22)$$

we obtain

$$\left(\frac{\partial x_j}{\partial n_j}\right)_{n_i, Q_x} = \left(\frac{\partial x_j}{\partial n_j}\right)_{n_i, \zeta} + \left(\frac{\partial x_j}{\partial \zeta}\right)_{n_j} \left(\frac{\partial \zeta}{\partial n_j}\right)_{n_i, Q_x} \quad (23)$$

If  $Q_x$  is fixed at  $K_x$ , Eq. 23 will characterize an equilibrium system. The term  $\left(\frac{\partial x_j}{\partial n_j}\right)_{n_i, \zeta}$  on the right of Eq. 23 means that  $x_j$  is increased when  $A_j$  is added into an equilibrium system when the system is frozen since

$$\left(\frac{\partial x_j}{\partial n_j}\right)_{n_i, \zeta} = \frac{1 - x_j}{n_T} > 0 \tag{24}$$

Equation 24 is represented by the movement from (1) to (2) in Fig. 2. The term  $\left(\frac{\partial x_j}{\partial \zeta}\right)_{n_j} \left(\frac{\partial \zeta}{\partial n_j}\right)_{n_i, Q_x}$  on the right of Eq. 23 represents the effect of the equilibrium shift and is shown by the movement from (2) to (3) in Fig. 2. Since

$$Q_x = Q_x(n_j, \zeta) = Q_x[n_j, \zeta(n_j, \Delta G)] = Q_x[n_j, \zeta(n_j, K_x)] \tag{25}$$

We obtain

$$dQ_x = \left(\frac{\partial Q_x}{\partial n_j}\right)_{n_i, \zeta} dn_j + \left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_i} d\zeta \tag{26}$$

For equilibrium  $dQ_x = 0$  we obtain

$$\left(\frac{\partial \zeta}{\partial n_j}\right)_{n_i, Q_x} = -\frac{\left(\frac{\partial Q_x}{\partial n_j}\right)_{\zeta, n_i}}{\left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_i}} \tag{27}$$

Equation 27 implies that  $\left(\frac{\partial \zeta}{\partial n_j}\right)_{n_i, Q_x}$  and  $\left(\frac{\partial Q_x}{\partial n_j}\right)_{\zeta, n_i}$  have opposite signs since  $\left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_i}$  is positive. Inserting Eq. 27 into Eq. 23

$$\begin{aligned} \left(\frac{\partial x_j}{\partial n_j}\right)_{n_i, Q_x} &= \left(\frac{\partial x_j}{\partial n_j}\right)_{n_i, \zeta} + \left(\frac{\partial x_j}{\partial \zeta}\right)_{n_j} \left(\frac{\partial \zeta}{\partial n_j}\right)_{n_i, Q_x} \\ &= \left(\frac{\partial x_j}{\partial n_j}\right)_{n_i, \zeta} - \left(\frac{\partial x_j}{\partial \zeta}\right)_{n_j} \frac{\left(\frac{\partial Q_x}{\partial n_j}\right)_{n_i, \zeta}}{\left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_i}} \end{aligned} \tag{28}$$

Since [15]

$$\begin{aligned} \left(\frac{\partial x_j}{\partial \zeta}\right)_{n_j} &= \left(\frac{\partial}{\partial \zeta} \frac{n_j^0 + v_j \zeta}{\left(\sum_{i=1}^N n_i^0\right) + \zeta \Delta v}\right)_{n_j} = \left(\frac{v_j}{n_T} - \frac{n_j \Delta v}{n_T^2}\right) \\ &= \left(\frac{v_j - \Delta v x_j}{n_T}\right) = x_j \left(\frac{v_j}{n_j} - \frac{\Delta v}{n_T}\right) \end{aligned} \tag{29}$$

from Eqs. 16, 28, and 29 we obtain Eq. 30 by reference to Eq. 5.

$$\begin{aligned} - \left( \frac{\partial x_j}{\partial \zeta} \right)_{n_j} \frac{\left( \frac{\partial Q_x}{\partial n_j} \right)_{n_i, \zeta}}{\left( \frac{\partial Q_x}{\partial \zeta} \right)_{n_i}} &= - \frac{v_j - x_j \Delta v}{n_T} \frac{Q_x \frac{v_j - x_j \Delta v}{n_j}}{\left( \frac{\partial Q_x}{\partial \zeta} \right)_{n_i}} \\ &= - \frac{Q_x (v_j - x_j \Delta v)^2}{n_j n_T \left( \frac{\partial Q_x}{\partial \zeta} \right)_{n_i}} \leq 0 \end{aligned} \quad (30)$$

Equation 30 signifies that  $\left( \frac{\partial x_j}{\partial \zeta} \right)_{n_j}$  and  $\left( \frac{\partial \zeta}{\partial n_j} \right)_{n_i, Q_x = K_x}$  have opposite signs and their product represents the counteraction to the change represented by Eq. 24. The result from Eqs. 28 and 30 is shown by the movement from (2) to (3) in Fig. 2. The term  $\left( \frac{\partial x_j}{\partial n_j} \right)_{n_i, Q_x}$  on the left side of Eq. 28 is represented by the movement from (1) to (3) in Fig. 2 [16] since

$$\left( \frac{\partial x_j}{\partial n_j} \right)_{n_i, Q_x} \geq 0 \quad (31)$$

The conclusions implied in Fig. 2 can only be justified by the necessary mathematics in Eqs. 24, 30 and 31. Equation 24 describes the movement from (1) to (2) in Fig. 2 for the addition while the counteraction represented by Eq. 30 describes the movement from (2) to (3) for the response of the reaction and Eq. 31 describes the movement from (1) to (3) for the initial and final states. The equals sign in Eq. 31 indicates the special case where (1) and (3) are at the same level. It can be seen in Fig. 2 that the equilibrium shift does not refer to the movement from (2) to (3) since  $Q_x$  is not equal to  $K_x$  for (2). Only the movement from (1) to (3) refers to equilibrium shift since both starting and ending states are equilibrium states and both states satisfy the condition that  $Q_x = K_x$ . However, the equilibrium shift from (1) to (3) only invokes a chemical reaction from (2) to (3) since the reaction is frozen from (1) to (2).

The mathematics shows convincingly that even when the equilibrium is shifted to produce more of the added species, the concentration of that species is decreased by the shift from (2) to (3) in Fig. 2. This difficult concept can only be accepted vaguely without the help of mathematics. For example there are many ambiguous concepts expressed in the literature of chemical equilibrium because rigorous mathematics is not introduced. We have come across statements from well-regarded authors such as “if the number of moles of products in a balanced chemical equation for a gaseous equilibrium system is not equal to the number of moles of reactants, adding more reactant at constant pressure and temperature may further raise rather than partially offset the increase in concentration of that reactant.” [5]. This apparently means that  $x_{N_2}$  was increased by the equilibrium shift characterized from (2) to (3) in Fig. 2 that produces more added  $N_2$  in Eq. 1 which is demonstrably wrong from the above analysis. Indeed the correct statement should be that the equilibrium always partially offsets the increase in concentration of the added species as shown in the process from (2) to (3) in Fig. 2 but can never raise further the concentration of that species even

though the added species is produced by such a shift. Or, consider this statement: “One of the most reported limitations of the principle (referring to Le Chatelier’s principle) has been its inability to appreciate that an increase in mass does not always imply an increase in concentration.” [31]. In other words, the statement means that the concentration of  $N_2$  could have been decreased by an increase in mass of  $N_2$  from adding more  $N_2$ .<sup>4</sup> However, as shown by Eq. 24, the concentration of  $N_2$  is increased as  $N_2$  is added (the mass of  $N_2$  is increased) when the reaction is frozen. What is more, when considering the process from (1) to (3) in Fig. 2, this statement is clearly wrong since Eq. 31 shows that the new equilibrium concentration  $x_{N_2}$  after  $N_2$  is added (the mass of  $N_2$  is increased) can never become lower than the original equilibrium concentration. When the reaction shifts backward,  $n_{N_2}$  is increased (the mass of  $N_2$  is indeed increased) and this effect increase  $x_{N_2}$  instead of decrease  $x_{N_2}$  as stated in effect (b) in Theorem 2iv. The backward reaction reduces  $x_{N_2}$  from (2) to (3) in Fig. 2 and Table 2 not because  $n_{N_2}$  is increased (the mass of  $N_2$  is increased), but it is caused by the increase in  $n_T$  as stated in effect (a) in Theorem 2iv.

The discussion above shows that the results from mathematics are rigorous and helpful. The qualitative presentation of the conclusions implied in Fig. 2 is often obscure and confusing. i.e. the phrase “equilibrium shift” might refer to either the movement from (1) to (3) or the result of counteraction from (2) to (3) in Fig. 2. But using mathematical language, the meaning can be clearly expressed without any ambiguity. The conclusions obtained from Eqs. 24, 30, and 31 and represented in Fig. 2 can be generalized as demonstrated below.

An inert system at temperature  $T_1$  absorbs a definite amount of heat to reach a new temperature  $T_2$ . This is equivalent to the result represented by Eq. 24 or the movement from (1) to (2) in Fig. 2. However, in an alternative system with a chemical equilibrium of an endothermal or exothermal reaction at  $T_1$  which absorbs the same amount of heat, the chemical equilibrium shift will reduce the change in  $T_2$  compared with the original inert system. This is equivalent to the result represented by Eq. 30 or the movement from (2) to (3) in Fig. 2. Note that under special conditions the equilibrium can shift to such an extent that the final  $T_2$  is reduced to the initial  $T_1$  which is equivalent to the case when the equal sign is valid in Eq. 31. But the equilibrium cannot shift further to make  $T_2$  lower than  $T_1$  since the less than sign is not valid in Eq. 31. Thus, the implications of Eqs. 24, 30, and 31 and Fig. 2 are general and can be summarized in Theorem 3 for a pair of conjugated variables [8, 16].

**Theorem 3** *The change of an intensive variable caused by changing its conjugated extensive variable is smaller if chemical equilibrium is maintained than if no reaction can take place in the system; (b) the change of an extensive variable caused by changing its conjugated intensive variable will be larger if chemical equilibrium is maintained*

<sup>4</sup> This statement is consistent with the fact that a backward reaction can be initiated by adding  $N_2$  such as that given in Eq. 1. However the statement is not correct to imply that initiating a backward reaction signifies that the concentration of  $N_2$  has been reduced by adding  $N_2$  and that in order to counteract the decrease in concentration, the backward reaction has been initiated; or that the concentration of  $N_2$  is increased by the addition and it initiates a backward reaction to reduce  $x_{N_2}$  because the amount of  $N_2$  is increased. Confused concepts like this occur because rigorous mathematical language has not been used.

than if no reaction can take place in the system; (c) however, the theorem cannot be applied to pair of non-conjugated variables.

Theorem 3 originates naturally from the mathematical discussion above. From Eqs. 28 and 30 we obtain Eq. 32 for the intensive variable  $x_j$

$$\left| \left( \frac{\partial x_j}{\partial n_j} \right)_{n_i, Q_x} \right| \leq \left| \left( \frac{\partial x_j}{\partial n_j} \right)_{n_i, \zeta} \right| \quad (32)$$

and obtain Eq. 33 for the extensive variable  $n_j$  corresponding to  $x_j$

$$\left| \left( \frac{\partial n_j}{\partial x_j} \right)_{n_i, Q_x} \right| \geq \left| \left( \frac{\partial n_j}{\partial x_j} \right)_{n_i, \zeta} \right| \quad (33)$$

Like Eqs. 32 and 33, a pair of conjugated variables, intensive  $Z$  and its corresponding conjugated extensive  $z$ , can be expressed in partial derivatives as those in Eqs. 34 and 35 [17].

$$\left| \left( \frac{\partial Z}{\partial z} \right)_{Q_x} \right| \leq \left| \left( \frac{\partial Z}{\partial z} \right)_{\zeta} \right| \quad (34)$$

$$\left| \left( \frac{\partial z}{\partial Z} \right)_{Q_x} \right| \geq \left| \left( \frac{\partial z}{\partial Z} \right)_{\zeta} \right| \quad (35)$$

Equations 34 and 35 imply that equilibrium always shifts to reduce the change in intensive variables and enhance the change in extensive variables of a pair of conjugated variables [8]. The generalization in Eqs. 34 and 35 is validated by a mathematical principle implied in Eqs. 36–40 [15]. For a pair of conjugated variables  $Z$  and  $z$

$$Z = f(z, \zeta) \quad (36)$$

then

$$dZ = \left( \frac{\partial f}{\partial z} \right)_{\zeta} dz + \left( \frac{\partial f}{\partial \zeta} \right)_{z} d\zeta \quad (37)$$

When  $d\zeta$  is caused by  $dz$  in Eq. 37, we obtain Eqs. 38 and 39. It has been shown that Eq. 38 is true when  $\left( \frac{\partial f}{\partial z} \right)_{\zeta}$  is positive and 38' is true when  $\left( \frac{\partial f}{\partial z} \right)_{\zeta}$  is negative for any pair of conjugated variables [17].

$$\left( \frac{\partial f}{\partial z} \right)_{\zeta} + \left( \frac{\partial f}{\partial \zeta} \right)_{z} \left( \frac{\partial \zeta}{\partial z} \right)_{Q_x} \geq 0 \quad (38)$$

$$\left(\frac{\partial f}{\partial z}\right)_\zeta + \left(\frac{\partial f}{\partial \zeta}\right)_z \left(\frac{\partial \zeta}{\partial z}\right)_{Q_x} \leq 0 \tag{38'}$$

From Eqs. 38 and 38' we obtain Eq. 39 for positive values of  $\left(\frac{\partial Z}{\partial z}\right)_\zeta$  and Eq. 39' for negative values of  $\left(\frac{\partial Z}{\partial z}\right)_\zeta$ .

$$\left(\frac{\partial Z}{\partial z}\right)_\zeta \geq -\left(\frac{\partial Z}{\partial \zeta}\right)_z \left(\frac{\partial \zeta}{\partial z}\right)_{Q_x} \tag{39}$$

$$\left(\frac{\partial Z}{\partial z}\right)_\zeta \leq -\left(\frac{\partial Z}{\partial \zeta}\right)_z \left(\frac{\partial \zeta}{\partial z}\right)_{Q_x} \tag{39'}$$

For the extreme case where the equal sign is satisfied in both Eqs. 39 and 39', we obtain

$$\left(\frac{\partial Z}{\partial \zeta}\right)_z \left(\frac{\partial \zeta}{\partial z}\right)_z \left(\frac{\partial z}{\partial Z}\right)_\zeta = -1 \tag{40}$$

What is common in Eqs. 39 and 39' is that  $\left(\frac{\partial Z}{\partial z}\right)_\zeta$  and  $\left(\frac{\partial Z}{\partial \zeta}\right)_z \left(\frac{\partial \zeta}{\partial z}\right)_z$  have opposite signs and this relationship remains in Eq. 40. Equation 40 is the case where the equal sign is taken in both Eqs. 39 and 39' and thus the discussion can only refer to Eq. 41 which is another form of Eq. 40.

$$\left(\frac{\partial Z}{\partial z}\right)_{Q_x} = \left(\frac{\partial Z}{\partial z}\right)_\zeta + \left(\frac{\partial Z}{\partial \zeta}\right)_z \left(\frac{\partial \zeta}{\partial z}\right)_{Q_x} = 0 \tag{41}$$

In Eq. 41 the value of  $\left(\frac{\partial Z}{\partial z}\right)_\zeta$  can be negative or positive [16,17]. However, as indicated in Eqs. 39 and 39',  $\left(\frac{\partial Z}{\partial z}\right)_\zeta$  is always opposite in sign and larger in absolute value than  $\left(\frac{\partial Z}{\partial \zeta}\right)_z \left(\frac{\partial \zeta}{\partial z}\right)_{Q_x}$  thus  $\left(\frac{\partial Z}{\partial \zeta}\right)_z \left(\frac{\partial \zeta}{\partial z}\right)_{Q_x}$  represents the counteraction to the change represented by  $\left(\frac{\partial Z}{\partial z}\right)_\zeta$ .

The terms  $\left(\frac{\partial Q_x}{\partial n_j}\right)_{\zeta, n_i}$  and  $\left(\frac{\partial \zeta}{\partial n_j}\right)_{n_i, Q_x=K_x}$  have opposite signs from Eqs. 5 and 27. Thus, if  $Q_x$  has a maximum, then  $\zeta$  must have a minimum. When adding a reactant j if  $\Delta v > 0$  (the added species on the side with smaller sum of coefficients),  $\left(\frac{\partial Q_x}{\partial n_j}\right)_{\zeta, n_i}$  is negative from Eq. 16 and  $\left(\frac{\partial \zeta}{\partial n_j}\right)_{n_i, Q_x=K_x}$  is positive from Eq. 27. When adding the reactant j if  $\Delta v < 0$ ,  $\left(\frac{\partial Q_x}{\partial n_j}\right)_{\zeta, n_i}$  is negative and  $\left(\frac{\partial \zeta}{\partial n_j}\right)_{n_i, Q_x=K_x}$  is positive when  $x_j < \frac{v_j}{\Delta v}$ . The reaction proceeds to consume the added reactant. According to Eq. 31,  $x_j$  increases as j is added. When  $x_j > \frac{v_j}{\Delta v}$ ,  $\left(\frac{\partial Q_x}{\partial n_j}\right)_{\zeta, n_i}$  is positive and  $\left(\frac{\partial \zeta}{\partial n_j}\right)_{n_i, Q_x=K_x}$

is negative. The reaction proceeds to produce more of the added reactant. Thus at  $x_j = \frac{v_j}{\Delta v}$ ,  $Q_x$  has a minimum and  $\zeta$  has a maximum as  $n_j$  is increased if  $\Delta v < 0$  and  $v_j < 0$  while  $Q_x$  has a maximum and  $\zeta$  has a minimum as  $n_j$  is increased if  $\Delta v > 0$  and  $v_j > 0$  [30].

The fact that  $\left(\frac{\partial \zeta}{\partial n_j}\right)_{Q_x=K_x}$  and  $\left(\frac{\partial x_j}{\partial \zeta}\right)_{n_j}$  have opposite signs, signified by Eqs. 16, 27 and 29, is consistent with Theorem 3. The addition of  $j$  to a gaseous equilibrium at constant  $T$  and  $P$ , whether  $j$  is a reactant or a product, will initiate an equilibrium displacement that decreases the conjugated intensive variable  $x_j$  stipulated in Theorem 3. If  $\left(\frac{\partial x_j}{\partial \zeta}\right)_{n_j} < 0$  at the time of addition, a forward reaction is initiated to reduce the intensive variable, with the result that  $\left(\frac{\partial \zeta}{\partial n_j}\right)_{Q_x=K_x} > 0$ . Similarly, if  $\left(\frac{\partial x_j}{\partial \zeta}\right)_{n_j} > 0$  a backward reaction is initiated to reduce the intensive variable, with the result that  $\left(\frac{\partial \zeta}{\partial n_j}\right)_{Q_x=K_x} < 0$  conforming with Theorem 3 and the fact that the two derivatives have opposite signs. Since the relationship between  $x_j$  and  $\zeta$  in Eq. 29 is correlated with the relationship between  $Q_x$  and  $n_j$  in Eq. 16, the condition that the forward reaction increases  $x_j$   $\left(\left(\frac{\partial x_j}{\partial \zeta}\right)_{n_j} > 0\right)$  is correlated with the fact that the addition of  $j$  leads to an increase in  $Q_x$   $\left(\left(\frac{\partial Q_x}{\partial n_j}\right)_{\zeta, n_i} > 0\right)$ , both initiating a backward reaction. i.e.  $x_j$  correlates to  $Q_x$  and  $\zeta$  correlates to  $n_j$ ; indeed how  $x_j$  increases with  $\zeta$  correlates to how  $Q_x$  increases with  $n_j$ . Thus Theorem 3 is correlated with Theorem 2. For example, if the added species  $j$  is a reactant ( $v_j < 0$ ), then from Eq. 29  $\left(\frac{\partial x_j}{\partial \zeta}\right)_{n_j} < 0$  when  $\frac{v_j}{\Delta v} < 0$ , and when both  $\frac{v_j}{\Delta v} > 0$  and  $x_j < \frac{v_j}{\Delta v}$ . A forward reaction will result from both Theorems 3 and 2, i.e. the addition of reactant  $j$  results in a forward reaction with  $\left(\frac{\partial \zeta}{\partial n_j}\right)_{Q_x=K_x} > 0$ . On the other hand  $\left(\frac{\partial x_j}{\partial \zeta}\right)_{n_j} > 0$  when  $\frac{v_j}{\Delta v} > 0$  and  $x_j > \frac{v_j}{\Delta v}$ , and then a backward reaction will result from both the two theorems resulting in  $\left(\frac{\partial \zeta}{\partial n_j}\right)_{Q_x=K_x} < 0$ . The same discussion applies if  $j$  is a product. Equation 29, which is similar to Eq. 72 in Appendix 2, can be derived from Eq. 42.<sup>5</sup>

$$x_j(\zeta + d\zeta) = \frac{n_j + v_j d\zeta}{n_T + \Delta v d\zeta} = x_j \frac{1 + \frac{v_j d\zeta}{n_j}}{1 + \frac{\Delta v d\zeta}{n_T}} \quad (42)$$

The relationship between Theorems 2 and 3 becomes even more explicit with the following treatment which is similar to that detailed in “Appendix 2”.  $x_j$  can be reduced by decreasing its numerator  $n_j$  or increasing its denominator  $n_T$ . Let the added species  $j$  be a product where  $v_j > 0$ . From Eq. 42 the forward reaction will increase the numerator  $n_j$  and decrease the denominator  $n_T$  of  $x_j$  when  $\Delta v < 0$  or  $\frac{v_j}{\Delta v} < 0$ , so that both the numerator and denominator of  $x_j$  will change to increase  $x_j$  by increasing  $\zeta$ ,

<sup>5</sup> The correct form of Eq. 21 in Ref. [16] should be Eq. 42 presented here. We also note that the last terms in Eqs. 94 and 95 of Ref. [15] should be  $(\lambda a_i - b_i)^2 \geq 0$  and  $\sum_i (\lambda a_i - b_i)^2 \geq 0$ , respectively.



resulting in  $\left(\frac{\partial x_j}{\partial \zeta}\right)_{n_j} > 0$ . Thus a backward reaction is anticipated from both Theorem 3 and corollaries ii and iv of Theorem 2, resulting in  $\left(\frac{\partial \zeta}{\partial n_j}\right)_{Q_x=K_x} < 0$ . By Eq. 42 the change in numerator dominates the change in  $x_j$  when  $x_j < \frac{v_j}{\Delta v}$  if  $\Delta v > 0$  or  $\frac{v_j}{\Delta v} > 0$ , conforming to Theorem 2 and resulting in  $\left(\frac{\partial x_j}{\partial \zeta}\right)_{n_j} > 0$ . According to Theorem 3,  $x_j$  needs to be reduced. A backward reaction is thus initiated since it reduces the numerator of  $x_j$ , resulting in  $\left(\frac{\partial \zeta}{\partial n_j}\right)_{Q_x=K_x} < 0$ . The validity of Theorems 2 and 3 can similarly be verified if the added species  $j$  is a reactant where  $v_j < 0$ .

As stated in Theorem 2, whether the added species  $j$  is a product ( $v_j > 0$ ) or a reactant ( $v_j < 0$ ), the change in denominator has an dominant effect on  $x_j$  when  $x_j > \frac{v_j}{\Delta v}$ , resulting in  $\left(\frac{\partial x_j}{\partial \zeta}\right)_{n_j} < 0$  for the added product and  $\left(\frac{\partial x_j}{\partial \zeta}\right)_{n_j} > 0$  for the added reactant. According to Theorem 3, a forward reaction will be initiated when the added species is a product, resulting in  $\left(\frac{\partial \zeta}{\partial n_j}\right)_{Q_x=K_x} > 0$ , and a backward reaction when the added species is a reactant, resulting in  $\left(\frac{\partial \zeta}{\partial n_j}\right)_{Q_x=K_x} < 0$ , since  $x_j$  is needed to be decreased by increasing its denominator  $n_T$ . Thus, the equilibrium shifts to increase the amount of  $j$  when  $j$  is added into a chemical equilibrium system if  $x_j > \frac{v_j}{\Delta v}$ . Whether the equilibrium is shifted to reduce or increase the added species  $j$ ,  $x_j$  is always decreased (Theorem 3). The reaction direction anticipated from Theorems 2 and 3 is the same and the sign of  $\left(\frac{\partial \zeta}{\partial n_j}\right)_{Q_x=K_x}$  is opposite to that of  $\left(\frac{\partial x_j}{\partial \zeta}\right)_{n_j}$  in all circumstances.

When the intensive variable in Theorem 3 is referenced to the chemical potential  $\mu_j$  for species  $j$ , we obtain

$$\mu_j = \mu_j^0(T) + RT \ln P_j \tag{43}$$

where  $\mu_j^0(T)$  is the standard chemical potential at  $T$  and  $x_j$  is the mole fraction for species  $j$ . From Eqs. 29 and 44 we obtain Eq. 45.

$$P_j = P x_j \tag{44}$$

$$\left(\frac{\partial P_j}{\partial \zeta}\right)_{P, n_i} = P \frac{v_j - x_j \Delta v}{n_T} \tag{45}$$

As can be seen from Eqs. 43 to 45, the counteraction for  $\mu_j$  (Theorem 3) is equivalent to the counteraction for  $P_j$ , the partial pressure for species  $j$ . When  $x_j > \frac{v_j}{\Delta v}$  if  $v_j > 0$  and  $\Delta v > 0$ , the effect from  $n_T$  by  $\left(-P \frac{x_j \Delta v}{n_T}\right)$  is dominant according to Theorem 2 and then Eq. 46 is valid.

$$\left(\frac{\partial P_j}{\partial \zeta}\right)_{P, n_i} < 0 \tag{46}$$

Equation 46 signifies that a forward reaction can reduce  $P_j$  and also  $\mu_j$ , i.e. adding a product  $j$  at these conditions will result in an equilibrium shift to produce more  $j$  according to Theorem 3b in reducing  $P_j$ . When  $x_j > \frac{v_j}{\Delta v}$ , if  $v_j < 0$  and  $\Delta v < 0$ , then Eq. 47 pertains

$$\left(\frac{\partial P_j}{\partial \zeta}\right)_{P, n_i} > 0 \quad (47)$$

Equation 47 means that a backward reaction can reduce  $P_j$ . Thus adding a reactant  $j$  at these conditions will result in an equilibrium shift to produce more  $j$  which conforms to Theorem 3. In the above cases, the equilibrium shift changes direction at  $x_j = \frac{v_j}{\Delta v} > 0$ .

Since

$$x_j = \frac{n_j}{n_T} = \frac{v_j}{\Delta v} > 0 \quad (48)$$

using Eqs. 48–50 we obtain Eq. 51.

$$n_j = n_j^0 + v_j \zeta \quad (49)$$

$$n_T = \left(\sum_i n_i^0\right) + \Delta v \zeta \quad (50)$$

$$\frac{n_j^0}{\sum_{i \neq j} n_i^0} = \frac{v_j}{\sum_{i \neq j} v_i} > 0 \quad (51)$$

From Eq. 51 we obtain

$$\frac{n_j^0}{n_j^0 + \sum_{i \neq j} n_i^0} = \frac{v_j}{v_j + \sum_{i \neq j} v_i} > 0 \quad (52)$$

or

$$x_j = \frac{n_j^0}{n_j^0 + \sum_{i \neq j} n_i^0} = \frac{v_j}{v_j + \sum_{i \neq j} v_i} > 0 \quad (53)$$

Equation 48 is expressed in mole fractions while Eq. 51 is expressed using the initial number of moles but the two equations are essentially equivalent (a consequence of Theorem 5 from Ref. [15]). The equilibrium shift will go in different directions when  $x_j$  is smaller or larger than the value indicated in Eq. 53 or when the initial mole ratio is smaller or larger than the value indicated in Eq. 51. In Eq. 1 the equilibrium changes direction at  $w = 1$  confirming the result shown in Eq. 51 as  $\frac{w}{1} = \frac{n_{N_2}^0}{n_{H_2}^0 + n_{NH_3}^0} = \frac{v_{N_2}}{v_{NH_3} + v_{H_2}} = \frac{-1}{2-3} = 1$  which is equivalent to Eq. 48 as  $x_j = \frac{v_j}{\Delta v} = 0.5$ .

The condition for  $\left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_i} = 0$  (Corollary 1 in Theorem 1) and for maximizing the mole fraction of a target product (Theorem 6 in [15]) is

$$\frac{n_j}{n_i} = \frac{v_j}{v_i} > 0 \quad (54)$$

Equation 55 (relevant to Theorem 5 in [15]) can be obtained from 54 using Eq. 49.

$$\frac{n_j^0}{n_i^0} = \frac{v_j}{v_i} > 0 \quad (55)$$

In fact if the initial mole ratio satisfies Eq. 55, then Eq. 54 is guaranteed to be valid at any time with any value of  $\zeta$  as shown by Eq. 56. i.e. if the ratio of the initial amounts of moles for the reacting species is equal to the ratio of their coefficients in the balanced chemical reaction, then this will guarantee that the ratio of the amounts of moles at any time will be equal to the ratio of their coefficients.

$$\frac{n_j}{n_i} = \frac{n_j^0 + v_j \zeta}{n_i^0 + v_i \zeta} = \frac{v_j}{v_i} = \frac{n_j^0}{n_i^0} \quad (56)$$

Equation 54 is correlated with Eq. 48 by Eq. 52 and there are a number of similar correlations in the mathematics related with chemical equilibrium [16]. As shown above, many of the relationships in chemistry can only be understood via detailed mathematical analysis.

## 5 Conclusions

Le Chatelier's principle has been successfully applied to many cases in chemistry. However, it can fail in a number of situations. It is shown in Sect. 2 that this failure cannot be corrected within the original framework of the principle and it is then confirmed by a numerical evaluation in Sect. 3 that the application of the principle fails for gaseous reaction systems at constant T and P but might be less problematic for systems at constant volume. Finally a general theoretical system is developed based on the principles developed in this series of publications [15–17]. It is pointed out through Eq. 15 that there are often differences between mathematical chemistry and pure mathematics. However, rigorous mathematical analysis is usually relevant to chemistry.

It must be realized that Le Chatelier's principle was not created in a formal mathematical context as mathematical knowledge in the late nineteenth century was not as advanced as now. There have been recent attempts to reformulate the principle [8] but such efforts lead to completely different sets of rules. The lesson from this work is that the popularly accepted view of the merits of Le Chatelier's principle deserves a significant and thorough reevaluation.

It is surprising that there remain difficulties in presenting equilibrium concepts in modern chemistry [5]. It is even more surprising when it is considered that the

difficulties can readily be overcome by introducing a disciplined elementary mathematical treatment in elementary chemistry courses but even so this has not been done, especially in the field of chemical education, or indeed in the classroom [5]. All the mathematical tools applied in this work are appropriate for the equilibrium theory so that it is surprising that such treatment has not yet been introduced into the education system. In fact, more rigorous and abstract understanding should be the real pursuit of scientific research and elementary chemistry needs to be modernized beyond taxonomy and rote learning by introducing more mathematics.

Some chemists reject theoretical and mathematical treatments since they consider chemistry as an experimental science [32]. Indeed some chemists consider that avoiding mathematics has advantages in gaining in concept understanding, motivation, and are not put off the subject by ‘difficult’ mathematics. Indeed there have been attempts to rewrite Le Chatelier’s principle in different ways without mathematics in order to conceal its inadequacies. However, mathematics helps to build a more rigorous, systematic, general, and abstract understanding.<sup>6</sup> Concepts developed from mathematical methods can only be understood from mathematics. It is shown from this work that conceptual understanding without mathematical analysis usually leads to superficial appreciation. There are many parts of chemistry like those introduced in this paper in which only a mathematical treatment can lead to real understanding [33,34].

## Appendices

### Appendix 1: Another proof for Theorem 1 with gaseous species on both sides of the chemical equation

It has been pointed out previously [15] that there is a mistake in the Proof of Theorem 1 by Katz [10]. The proof below corrects that mistake. Since

$$n_1^2 v_2^2 + n_2^2 v_1^2 \geq 2v_1 v_2 n_1 n_2 \quad (57)$$

We obtain

$$\frac{v_1^2}{n_1} + \frac{v_2^2}{n_2} \geq \frac{(v_1 + v_2)^2}{n_1 + n_2} \quad (58)$$

Equation 58 can also be obtained when Eq. 59 is valid.

$$\frac{n_2}{n_1} = \frac{v_2}{v_1} > 0 \quad (59)$$

$$\frac{v_1^2}{n_1} + \frac{v_2^2}{n_2} = \frac{(v_1 + v_2)^2}{n_1 + n_2} \quad (60)$$

<sup>6</sup> For example an anonymous reviewer correctly commented: “mathematical knowledge is generally highly valued in chemistry, and there are many research groups who apply it effectively and successfully.” and “The computer-based simulation and design tools used by practicing chemists and chemical engineers require significant mathematical/computational knowledge.”

$v_1$  and  $v_2$  in Eq. 59 are either both positive or negative since  $n_1$  and  $n_2$  are both positive. If  $v_1$  and  $v_2$  have opposite signs, the equal sign should be excluded in Eq. 58. Equation 60 can also be derived from Schwarz inequality 61.

$$\sum_{i=1}^N a_i^2 \sum_{i=1}^N b_i^2 \geq \left( \sum_{i=1}^N a_i b_i \right)^2 \tag{61}$$

Inequality 61 is equivalent to Eq. 62 [15].

$$\sum_{i=1}^N \sum_{j>i}^N (a_i b_j - a_j b_i)^2 \geq 0 \tag{62}$$

From Eq. 62 it is clear that the equals sign in Eq. 61 is valid when Eq. 63 is satisfied for all  $i$  and  $j$ . From Eq. 63 we know that the equals sign can be included in the Schwarz inequality 61 when the signs for  $a_i$  and  $b_i$  are the same, but not otherwise.

$$\frac{a_i}{b_i} = \frac{a_j}{b_j}, \quad i, j = 1, 2, 3, \dots, N \tag{63}$$

For example Eq. 61 is valid together with Eq. 64, i.e. including the equal sign.

$$a_i > 0, b_i > 0, \quad i = 1, 2, 3, \dots, N \tag{64}$$

When the signs for  $a_i$  and  $b_i$  are mixed, i.e. if some  $a_i$  has the same sign as its counterpart  $b_i$  while another  $a_j$  has the opposite sign to its counterpart  $b_j$ , Eq. 63 cannot be satisfied for all  $i$  and  $j$ , thus the equals sign in Eq. 61 should be excluded.

It can be demonstrated that Eq. 58 is one form of the Schwarz inequality shown by Eq. 61. If we define

$$a_i = \frac{|v_i|}{\sqrt{n_i}}, \quad b_i = \sqrt{n_i} \tag{65}$$

note  $n_i > 0$ . Equation 61 becomes

$$\sum_{i=1}^N \left| \frac{v_i}{\sqrt{n_i}} \right|^2 \sum_{i=1}^N n_i \geq \left( \sum_{i=1}^N |v_i| \right)^2 \tag{66}$$

Rearranging Eq. 66 we obtain Eq. 67 which is in a similar form to Eq. 58.

$$\sum_{i=1}^N \frac{v_i^2}{n_i} \geq \frac{\left( \sum_{i=1}^N |v_i| \right)^2}{\sum_{i=1}^N n_i} \tag{67}$$

Equation 67 is obtained by Katz [10] using mathematical induction. Both Eqs. 68 and 69 conform to the result implied by Eq. 67.

$$\sum_{i=1}^{N_p} \frac{v_{p_i}^2}{n_{p_i}} \geq \frac{\left(\sum_{i=1}^{N_p} v_{p_i}\right)^2}{\sum_{i=1}^{N_p} n_{p_i}} \quad (68)$$

$$\sum_{i=1}^{N=N_r} \frac{v_{r_i}^2}{n_{r_i}} \geq \frac{\left(\sum_{i=1}^{N=N_r} v_{r_i}\right)^2}{\sum_{i=1}^{N=N_r} n_{r_i}} \quad (69)$$

If there are gaseous species on both sides of the chemical equation, we obtain Eq. 70 since  $v_p$  and  $v_r$  have opposite signs.

$$\sum_{i=1}^{N=N_p+N_r} \frac{v_i^2}{n_i} > \frac{\left(\sum_{i=1}^{N=N_p+N_r} v_i\right)^2}{\sum_{i=1}^{N=N_p+N_r} n_i} = \frac{\Delta v^2}{n_T} \quad (70)$$

The validity of Eq. 70 can best be demonstrated by comparing it with Eq. 67 which is consistent with Eqs. 68 and 69 and was proposed by Katz [10], by using Eq. 71, i. e. because of Eq. 71, the equal sign in Eq. 70 has been excluded when there are gaseous species on both side of chemical equation.

$$\sum_{i=1}^N |v_i| > \sum_{i=1}^N v_i \quad (71)$$

Equation 70 conforms to Theorem 1 for the case when there are gaseous species on both sides of the chemical equation. It should be noted that Eq. 70 is correct in chemistry but not in mathematics since in the latter  $n_i$  can be negative.

## Appendix 2: Relevant mathematics for some aspects of Theorem 2

From Eq. 3 we obtain Eq. 72 for adding species  $j$  into a chemical system.

$$Q_x(n_j + dn_j) = \frac{\left(1 + \frac{v_j dn_j}{n_j}\right) \prod_{i=1}^N n_i^{v_i}}{\left(1 + \frac{\Delta v dn_j}{n_T}\right) n_T^{\Delta v}} \quad (72)$$

If we ignore the change in denominator  $D_x$  in Eq. 72, we obtain Eq. 74.

$$Q_x(n_j + dn_j)|_{D_x} = \left(1 + \frac{v_j dn_j}{n_j}\right) Q_x(n_j) \quad (73)$$

or

$$\Delta Q_x|_{D_x} = [Q_x(n_j + dn_j) - Q_x(n_j)]|_{D_x} = \frac{v_j dn_j}{n_j} Q_x(n_j) \quad (74)$$

If we ignore the change in numerator  $N_x$  in Eq. 72, we obtain Eq. 76.

$$\begin{aligned} Q_x(n_j + dn_j)|_{N_x} &= \frac{1}{\left(1 + \frac{\Delta v dn_j}{n_T}\right)} Q_x(n_j) \\ &= \left(1 + \frac{\Delta v dn_j}{n_T}\right)^{-1} Q_x(n_j) = \left(1 - \frac{\Delta v dn_j}{n_T}\right) Q_x(n_j) \end{aligned} \quad (75)$$

or

$$\Delta Q_x|_{N_x} = [Q_x(n_j + dn_j) - Q_x(n_j)]|_{N_x} = -\frac{\Delta v dn_j}{n_T} Q_x(n_j) \quad (76)$$

Parts (a) and (b) of Theorem 2 can be discussed along with Eq. 72. The discussion below is relevant to corollary ii of Theorem 2. From Eqs. 74 and 76,  $\Delta Q_x|_{D_x}$  and  $\Delta Q_x|_{N_x}$  have the same sign when  $v_j$  has an opposite sign to  $\Delta v$ , i.e. for the added species  $j$  on the side of chemical reaction with the smaller sum of coefficients. Thus the effects described in parts (a) and (b) shift the equilibrium in the same direction when  $\frac{v_j}{\Delta v} < 0$ . But if  $v_j$  and  $\Delta v$  have the same sign,  $\Delta Q_x|_{D_x}$  and  $\Delta Q_x|_{N_x}$  have opposite signs and the effects described in parts (a) and (b) shift the equilibrium in opposite directions.  $\Delta Q_x|_{D_x}$  overrides  $\Delta Q_x|_{N_x}$  when Eq. 77 is satisfied, i.e. the effect specified in Theorem 2b is dominant.

$$\left| \frac{v_j dn_j}{n_j} Q_x(n_j) \right| > \left| \frac{\Delta v dn_j}{n_T} Q_x(n_j) \right| \quad (77)$$

When both  $v_j$  and  $\Delta v$  are negative, we obtain Eqs. 78 and 79 from 77.

$$\frac{v_j}{n_j} < \frac{\Delta v}{n_T} \quad (78)$$

or

$$x_j = \frac{n_j}{n_T} < \frac{v_j}{\Delta v} > 0 \quad (79)$$

Thus, as specified in Theorem 2ii, the effect described by Theorem 2b is dominant when  $x_j < \frac{v_j}{\Delta v} > 0$ . Similarly, the effect described by Theorem 2a is dominant when  $x_j > \frac{v_j}{\Delta v} > 0$ . When both  $v_j$  and  $\Delta v$  are positive, a similar discussion can be invoked and the result is specified by Theorem 2ii.

### Appendix 3: A detailed mathematical account of conjugated variables

The common feature of conjugated variable pairs for  $x_j$  and  $n_j$ ,  $C_j$  and  $n_j$ , or  $P$  and  $V$  in Eqs. 80–82 [17] is that they contain a square term in

$$\left(\frac{\partial x_j}{\partial \zeta}\right)_{n_i} \left(\frac{\partial Q_x}{\partial n_j}\right)_{\zeta, n_i}, \left(\frac{\partial C_j}{\partial \zeta}\right)_{V, n_i} \left(\frac{\partial Q_C}{\partial n_j}\right)_{V, \zeta}, \text{ or } \left(\frac{\partial P}{\partial \zeta}\right)_{T, V} \left(\frac{\partial Q_P}{\partial V}\right)_{T, \zeta},$$

such as  $(v_j - \Delta v x_j)^2$  in Eq. 80,  $(v_j)^2$  in Eq. 81, and  $(\Delta v)^2$  in Eq. 82.

$$\begin{aligned} \left(\frac{\partial x_j}{\partial n_j}\right)_{T, P, Q_x = K_x} &= \left(\frac{\partial x_j}{\partial n_j}\right)_{\zeta} - \left(\frac{\partial x_j}{\partial \zeta}\right)_{n_i} \frac{\left(\frac{\partial Q_x}{\partial n_j}\right)_{\zeta, n_i}}{\left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_i}} \\ &= \frac{1 - x_j}{n_T} - \frac{v_j - \Delta v x_j}{n_T} \frac{Q_x \left(\frac{v_j - \Delta v x_j}{n_i}\right)}{\left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_i}^0} \geq 0 \end{aligned} \quad (80)$$

$$\begin{aligned} \left(\frac{\partial C_j}{\partial n_j}\right)_{T, V, Q_C = K_C} &= \left(\frac{\partial C_j}{\partial n_j}\right)_{\zeta} - \left(\frac{\partial C_j}{\partial \zeta}\right)_{V, n_i} \frac{\left(\frac{\partial Q_C}{\partial n_j}\right)_{V, \zeta}}{\left(\frac{\partial Q_C}{\partial \zeta}\right)_{V, n_i}} \\ &= \frac{1}{V} - \frac{v_j}{V} \frac{Q_C \frac{v_j}{n_j}}{Q_C \sum_{i=1}^N \frac{v_i^2}{n_i}} \geq 0 \end{aligned} \quad (81)$$

$$\begin{aligned} \left(\frac{\partial P}{\partial V}\right)_{T, Q_P = K_P} &= \left(\frac{\partial P}{\partial V}\right)_{T, \zeta} + \left(\frac{\partial P}{\partial \zeta}\right)_{T, V} \frac{\left(\frac{\partial Q_P}{\partial V}\right)_{T, \zeta}}{\left(\frac{\partial Q_P}{\partial \zeta}\right)_{T, V}} \\ &= -\frac{P}{V} - \frac{\Delta v P}{n_T} - \frac{\Delta v Q_P}{V} \frac{1}{Q_P \sum_{j=1}^N \frac{v_j^2}{n_j}} \leq 0 \end{aligned} \quad (82)$$

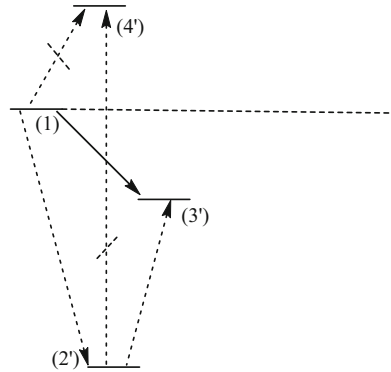
In Fig. 3, the shift from (1) to (2') represents  $\left(\frac{\partial P}{\partial V}\right)_{T, \zeta}$  in Eq. 82, while the shift from (2') to (3') is represented by the term  $\left(\frac{\partial P}{\partial \zeta}\right)_{T, V} \frac{\left(\frac{\partial Q_P}{\partial V}\right)_{T, \zeta}}{\left(\frac{\partial Q_P}{\partial \zeta}\right)_{T, V}}$ , and from (1) to (3') is the resultant derivative  $\left(\frac{\partial P}{\partial V}\right)_{T, Q_P = K_P}$ . (4') is a state inaccessible to the system which is indicated by  $\leq 0$  in Eq. 82.

On the other hand,  $x_k$  and  $n_j$  are not a pair of conjugated variables because there is not a square term in  $\left(\frac{\partial x_k}{\partial \zeta}\right)_{n_j} \left(\frac{\partial Q_x}{\partial n_j}\right)_{\zeta, n_i}$  as shown in Eq. 83.

$$\begin{aligned} \left(\frac{\partial x_k}{\partial n_j}\right)_{T, P, Q_x = K_x} &= \left(\frac{\partial x_k}{\partial n_j}\right)_{\zeta} - \left(\frac{\partial x_k}{\partial \zeta}\right)_{n_j} \frac{\left(\frac{\partial Q_x}{\partial n_j}\right)_{\zeta, n_i}}{\left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_i}} \\ &= \frac{-x_k}{n_T} - \frac{v_k - \Delta v x_k}{n_T} \frac{Q_x \left(\frac{v_j - \Delta v x_j}{n_j}\right)}{\left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_i}^0} \end{aligned} \quad (83)$$



**Fig. 3** A pictorial representation of the derivatives in Eq. 82



A result similar to Eq. 82 can also be derived from thermodynamics [8]. For example, function A is defined in Eq. 84 for a system with entropy S.

$$A(S, V, \zeta) = \sum_i v_i \mu_i \tag{84}$$

At equilibrium, we have

$$dA = \left(\frac{\partial A}{\partial S}\right)_{\zeta, V} dS + \left(\frac{\partial A}{\partial V}\right)_{S, \zeta} dV + \left(\frac{\partial A}{\partial \zeta}\right)_{S, V} d\zeta = 0 \tag{85}$$

From Eq. 85 we obtain Eq. 86.

$$\left(\frac{\partial \zeta}{\partial V}\right)_{S, A} = -\frac{\left(\frac{\partial A}{\partial V}\right)_{S, \zeta}}{\left(\frac{\partial A}{\partial \zeta}\right)_{S, V}} \tag{86}$$

Equation 88 is obtained from Eq. 87.

$$dU = TdS - PdV + Ad\zeta \tag{87}$$

$$\left(\frac{\partial P}{\partial \zeta}\right)_{S, V} = -\left(\frac{\partial A}{\partial V}\right)_{S, \zeta} \tag{88}$$

From Eq. 86 and 88 we obtain Eq. 89 from  $P = P[S, V, \zeta(S, V, A)]$ .

$$\begin{aligned} \left(\frac{\partial P}{\partial V}\right)_{S, A} &= \left(\frac{\partial P}{\partial V}\right)_{S, \zeta} + \left(\frac{\partial P}{\partial \zeta}\right)_{S, V} \cdot \left(\frac{\partial \zeta}{\partial V}\right)_{S, A} \\ &= \left(\frac{\partial P}{\partial V}\right)_{S, \zeta} + \left(\frac{\partial A}{\partial V}\right)_{S, \zeta} \frac{\left(\frac{\partial A}{\partial V}\right)_{S, \zeta}}{\left(\frac{\partial A}{\partial \zeta}\right)_{S, V}} \end{aligned} \tag{89}$$

There is a square term  $\left[ \left( \frac{\partial A}{\partial V} \right)_{S,\zeta} \right]^2$  in Eq. 89. From Eq. 90 [17] it can be seen that the term  $\left( \frac{\partial P}{\partial \zeta} \right)_{S,V} \cdot \left( \frac{\partial \zeta}{\partial V} \right)_{S,A}$  is positive in Eq. 89. It should be noticed that  $\left( \frac{\partial P}{\partial V} \right)_{S,\zeta}$  is negative. Although it can be proved from thermodynamics that the signs for  $\left( \frac{\partial P}{\partial V} \right)_{S,\zeta}$  and  $\left( \frac{\partial P}{\partial \zeta} \right)_{S,V} \cdot \left( \frac{\partial \zeta}{\partial V} \right)_{S,A}$  are opposite, only mathematics can prove Eq. 91.

$$\left( \frac{\partial A}{\partial \zeta} \right)_{S,V} > 0 \quad (90)$$

$$\left| \left( \frac{\partial P}{\partial V} \right)_{S,\zeta} \right| \geq \left| \left( \frac{\partial P}{\partial \zeta} \right)_{S,V} \cdot \left( \frac{\partial \zeta}{\partial V} \right)_{S,A} \right| \quad (91)$$

In fact any pair of variables in a thermodynamic function, such as S and T, P and V,  $\mu_i$  and  $n_i$ , and A and  $\zeta$  in Eq. 87 for internal energy  $U$  or for other thermodynamic functions as enthalpy H, Helmholtz free energy F, Gibbs free energy G are conjugated variables.

#### Appendix 4: Symbols used

P pressure of the system.

V volume of system.

T temperature of the system.

q heat absorbed in the system.

w in Eq. 1 is the initial mole number of  $N_2$ .

t time.

R in Eq. 19 is the universal gas constant.

$A_i$  in Eq. 2 is the chemical formula for species i in chemical reaction.

i and j indices for species in a system. r and p are used for reactant and product respectively. N is the total number of species in the reacting system.  $N_r$  and  $N_p$  are the total number of reactants and products, respectively.

$\zeta$  the reaction extent. It is defined as  $\zeta = \frac{n_i - n_i^0}{v_i}$  along with Eq. 1.

$v_i$  the coefficient for species i in a balanced chemical reaction. Its value is positive for product and negative for reactant

$\Delta v$  the sum of the coefficients for all species in a balanced chemical reaction.

$$\Delta v = \sum_i v_i = \sum_p v_p - \sum_r |v_r|.$$

$n_i$  the amount of species i while  $n_i^0$  is for initial mole number.  $n_i = n_i^0 + v_i \xi$ .

$n_T$  total amount of all species in chemical reacting system.  $n_T = \sum_i n_i = \Delta v \zeta +$

$$\sum_i n_i^0.$$

$x_i$  mole fraction for species i.  $x_i = \frac{n_i}{n_T}$ .

$Q_x$  reaction quotient expressed in mole fractions.  $Q_x = \prod_i x_i^{v_i} = n_T^{-\Delta v} \prod_i n_i^{v_i}$ . It is a unitless quantity. At equilibrium  $Q_x = K_x$ . When the reaction quotient is expressed in partial pressure,  $Q_p$  is used and the corresponding equilibrium constant is  $K_p$ .  $Q_c$  is expressed in molarities as shown in Eq. 21.  $N_x$  and  $D_x$  are related to  $Q_x$  and defined as  $N_x = \prod_i n_i^{v_i}$ ,  $D_x = \left(\frac{1}{n_T}\right)^{\Delta v}$ .

$K_x$  an equilibrium constant formulated from mole fractions for gaseous chemical reaction at constant T and P.

$K_p$  an equilibrium constant formulated from partial pressures for chemical reactions at constant T.

G Gibbs energy.

$\mu_j$  the chemical potential for species j.  $\mu_j^0(T)$  is the standard chemical potential at temperature T.

## References

1. D. Oxtoby, H.P. Gillis, A. Campion, *Principles of Modern Chemistry*, 7th edn. (Brooks/Cole, Belmont, 2012)
2. [http://en.wikipedia.org/wiki/Van\\_%27t\\_Hoff\\_equation](http://en.wikipedia.org/wiki/Van_%27t_Hoff_equation)
3. P. Atkins, J. de Paula, *Atkins' Physical Chemistry*, 8th edn. (Oxford University Press, Oxford, 2006)
4. R.G. Mortimer, *Physical Chemistry*, 3rd edn. (Elsevier Academic Press, Amsterdam, 2008), p. 216
5. D. Cheung, *J. Chem. Educ.* **86**, 514–518 (2009)
6. J. Gold, V. Gold, *Chem. Br.* **20**, 802–804 (1984)
7. M. Hillert, *J. Ph. Equilib.* **16**(5), 403–410 (1995)
8. J. de Heer, *J. Chem. Educ.* **34**, 375–380 (1957)
9. F.G. Helfferich, *J. Chem. Educ.* **62**, 305–308 (1985)
10. L. Katz, *J. Chem. Educ.* **38**, 375–377 (1961)
11. K. Posthumus, *Recueil des Travaux Chimiques des Pays-Bas* **52**(1), 25–35 (1933)
12. K. Posthumus, *Recueil des Travaux Chimiques des Pays-Bas* **53**(4), 308–311 (1934)
13. R. Hoffman, *Solids and Surface: A Chemist's View of Bonding in Extended Structures* (VCH Publishers, Inc, New York, 1988)
14. D.C. Young, *Computational Chemistry: A Practical Guide for Applying Techniques to Real-World Problems* (Wiley, New York, 2001)
15. Y. Liu, Y. Liu, M.G.B. Drew, *J. Math. Chem.* **51**, 715–740 (2013)
16. Y. Liu, Y. Liu, M.G.B. Drew, *J. Math. Chem.* **51**, 741–762 (2013)
17. Y. Liu, M.G.B. Drew, Y. Liu, *J. Math. Chem.* **52**(5), 1191–1200 (2014)
18. S. Fujita, *J. Math. Chem.* **53**, 1010–1053 (2015)
19. B. Bira, T.R. Sekhar, *J. Math. Chem.* **53**, 1162–1171 (2015)
20. Y. Liu, Y. Liu, M.G.B. Drew, *Coord. Chem. Rev.* **260**, 37–64 (2014)
21. Y. Liu, Y. Liu, M.G.B. Drew, *J. Math. Chem.* **51**, 503–531 (2013)
22. <http://qz.com/15156/to-win-the-nobel-prize-in-economics-it-helps-to-wield-math-lots-of-it/>
23. A. van der Schaft, S. Rao, B. Jayawardhana, *J. Math. Chem.* **53**(6), 1445–1458 (2015)
24. L.J. Sacks, *J. Chem. Educ.* **82**(7), 997 (2005)
25. A.P. Olujenyo, *Educ. Pract. Innov.* **1**, 13–16 (2014) <http://www.scipublish.com/journals/EPI/papers/154>
26. R. Battino, *J. Chem. Educ.* **69**(2), 135–137 (1992)
27. J.C.E. Editorial, *J. Chem. Educ.* **70**(7), 522 (1993)
28. A.A. Russell, *J. Chem. Educ.* **70**(7), 523–527 (1993)
29. Z.-K. Liu, J. Agren, M. Hillert, *Fluid Ph. Equilib.* **121**, 167–177 (1996)
30. Y. Liu, Y. Liu, X. Yang, *Huaxue Tongbao (Chemistry)* (3), 51–54 (1994) (in Chinese). <http://www.cnki.com.cn/Article/CJFDTotat-HXTB403.016.htm>
31. J. Quilez-Pardo, J.J. Solaz-poroos, *J. Res. Sci. Teach.* **32**(9), 939–957 (1995)
32. S.J. Hawkes, *J. Chem. Educ.* **81**(9), 1257 (2004)

33. Y. Liu, R. Tai, Y. Liu, Huaxue Jiaoyu (Chinese J. Chem. Educ.) **36**(6), 1–10 (2015) (in Chinese). <http://www.cnki.com.cn/Article/CJFDTOTAL-FXJJ201506001.htm>
34. Y. Liu, Y. Liu, Huaxue Jiaoxue (Educ. Chem.) **310**(1), 70–72 (2013) (in Chinese). <http://www.cnki.com.cn/Article/CJFDTotal-HXJX201301031.htm>