

A mathematical approach to chemical equilibrium theory for gaseous systems—II: extensions and applications

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Abstract Straightforward mathematical techniques are used innovatively to form a coherent theoretical system to deal with chemical equilibrium problems. For a systematic theory it is necessary to establish a system to connect different concepts. This paper shows the usefulness and consistence of the system by applications of the theorems introduced previously. Some theorems are shown somewhat unexpectedly to be mathematically correlated and relationships are obtained in a coherent manner. It has been shown that theorem 1 plays an important part in interconnecting most of the theorems. The usefulness of theorem 2 is illustrated by proving it to be consistent with theorem 3. A set of uniform mathematical expressions are associated with theorem 3. A variety of mathematical techniques based on theorems 1–3 are shown to establish the direction of equilibrium shift. The equilibrium properties expressed in initial and equilibrium conditions are shown to be connected via theorem 5. Theorem 6 is connected with theorem 4 through the mathematical representation of theorem 1.

Keywords Systematics · Traditional fields · Equilibrium theory · Chemical education

1 Introduction

Despite the fact that chemical equilibrium is a well-established field, when complicated phenomena are involved, conventional methods can be difficult to apply readily

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in a straightforward manner [1]. In particular it does not provide enough tools to deal with facts such as the equilibrium shift always initiates a reaction to decrease the concentration of added species even though more of that species might be produced by the shift. Many chemists are unaware that the equilibrium can shift to produce more added species. It is well-known that mathematical approaches can reveal the real nature of the chemistry behind phenomena and can facilitate the development of a theory to further expansion in different areas. We have introduced a novel theoretical system for chemical equilibrium in part I of this work [2] by introducing the following six theorems which can be readily explained via mathematical techniques.

1: *The reaction quotient never decreases as a reaction proceeds forward and never increases as the reaction proceeds backward.*

2a: *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.*

2b: *On increasing N_x by adding a reactive species if D_x were kept unchanged, the equilibrium would respond by shifting to the side of reducing the amount of that species.*

3a: *The chemical equilibrium will shift to reduce the change in an intensive variable caused by the change in its corresponding extensive variable; (3b) but will increase the change of an extensive variable caused by changing the corresponding intensive variable.*

4: *When a species is added to a system, the new equilibrium concentration of that species will always be increased.*

5: *A property of a chemical equilibrium for a closed system is independent of whether an amount of species i is expressed at time $t = 0$ or at any subsequent time t .*

6: *The optimum conditions for maximizing the mole fraction of a target product in a chemical reaction are that the ratios of the initial number of moles for reactants and products are, respectively, equal to the ratio of their coefficients in the balanced chemical equation.*

Detailed proofs of these six theorems are provided in Part I of this work [2]. In this present paper, some unexpected correlations revealed by mathematical application of these six theorems are discussed in depth. The usefulness of these theorems in understanding specific examples of chemical equilibrium is revealed mathematically. We first present a graphical representation of theorems 3 and 4, which gives a general overview of the complete system. Subsequently we include several examples which show how the theorems provide a variety of mathematical tools for the successful analysis of equilibrium problems. Some equations from Part I of this work are repeated here and referred to as Eq. I-n, where n is their designation in Part I. The context of each of these equations will be found in Part I.

2 Extension and application of the six theorems

2.1 A graphical representation of theorems 3 and 4

Our first illustration is based on graphical representations of theorems 3 and 4 and provides a chemical visualization of the mathematical system and facilitates an intuitive

understanding of our system. The mathematical basis of the graphical representations is discussed in detail. The relationship of Eqs. I-33–I-35 in paper I to theorem 3 is also discussed here.

$$\left(\frac{\partial x_i}{\partial \zeta}\right)_{n_i} \left(\frac{\partial \zeta}{\partial n_i}\right)_{Q_x} \left(\frac{\partial n_i}{\partial x_i}\right)_{\zeta} = -1 \tag{I-33}$$

$$\left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_j} \left(\frac{\partial \zeta}{\partial n_i}\right)_{K_x} \left(\frac{\partial n_i}{\partial Q_x}\right)_{\zeta, n_j} = -1 \tag{I-34}$$

$$\left(\frac{\partial P}{\partial \zeta}\right)_{S, V} \left(\frac{\partial \zeta}{\partial V}\right)_{S, A} \left(\frac{\partial V}{\partial P}\right)_{S, \zeta} = -1 \tag{I-35}$$

2.1.1 Correlation between theorem 3 and I-33 and I-34

In an equilibrium system, x_i , the mole fraction of species i can be presented by Eq. I-36.

$$x_i = x_i(n_i, \zeta) = x_i [n_i, \zeta(n_i, Q_x)] \tag{I-36}$$

where n_i , represents the amount of species i , ζ the reaction extent and Q_x the reaction quotient. On differentiation, while keeping Q_x equal to the equilibrium constant K_x , we obtain

$$\left(\frac{\partial x_i(n_i, \zeta(n_i, Q_x))}{\partial n_i}\right)_{Q_x} = \left(\frac{\partial x_i(n_i, \zeta(n_i, Q_x))}{\partial n_i}\right)_{\zeta} + \left(\frac{\partial x_i(n_i, \zeta(n_i, Q_x))}{\partial \zeta}\right)_{n_i} \left(\frac{\partial \zeta}{\partial n_i}\right)_{Q_x} \tag{I-42}$$

The first term on the right hand side of Eq. I-42, namely $\left(\frac{\partial x_i}{\partial n_i}\right)_{\zeta}$, represents the effect on the intensive variable x_i when the extensive variable n_i is changed while the reaction extent, ζ , is kept constant. i.e. the effect on x_i when i is added if the chemical reaction is frozen. This term is always greater than zero as shown in I-43, which is derived from the definition of x_i in Eq. I-5.

$$\left(\frac{\partial x_i}{\partial n_i^0}\right)_{\zeta} = \left(\frac{\partial \frac{n_i^0 + \nu_i \zeta}{(\sum_j n_j^0) + \Delta \nu \zeta}}{\partial n_i^0}\right)_{\zeta} = \frac{1 - x_i}{n_T} > 0 \tag{I-43}$$

Equation I-43 signifies an open system so that an increase in n_i from equilibrium will cause x_i to increase and this is shown graphically in Fig. 1 where x_i increases from (a) to (b). Alternatively a decrease in n_i by removing species i from the system will cause x_i to be decreased from (a) to (b') as shown in Fig. 2. Figures 1 and 2 also show other consequences of theorems 3 and 4 as will be demonstrated below.

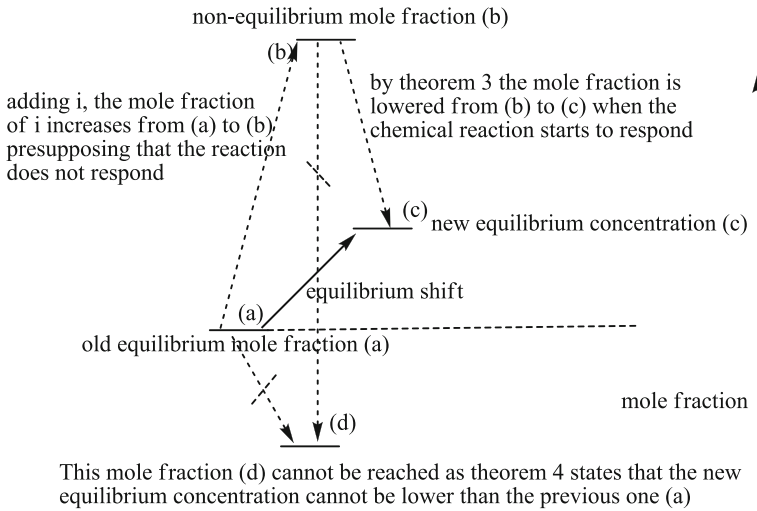


Fig. 1 A graphical representation of theorems 3 and 4. The figure describes what happens when species *i* is added to an equilibrium system. The *solid arrow* represents a real process from (a) to (c). It is equivalent to the combination of two processes from (a) to (b) and from (b) to (c) which are represented by *dotted lines*. Neither of these latter two processes can occur independently without the other. The line across a *dotted line* represents an impossible process. The mole fraction of *i* increases from (a) to (b) when *i* is added. By theorem 3, the intensive mole fraction x_i is decreased by chemical reaction, from (b) to (c). These two processes result in a final real equilibrium shift from (a) to (c). Theorem 4 states that the equilibrium shift can never reduce the mole fraction to (d), which is lower than (a), the initial mole fraction

The second term on the right hand side of Eq. I-42

$$\left(\frac{\partial x_i}{\partial n_i}\right)_{Q_x} = \left(\frac{\partial x_i}{\partial n_i}\right)_{\zeta} + \left(\frac{\partial x_i}{\partial \zeta}\right)_{n_i} \left(\frac{\partial \zeta}{\partial n_i}\right)_{Q_x} \tag{I-42}$$

namely $\left(\frac{\partial x_i}{\partial \zeta}\right)_{n_i} \left(\frac{\partial \zeta}{\partial n_i}\right)_{Q_x}$, represents the effect on x_i of a change of n_i when the chemical reaction begins to respond [from (b) to (c) represented in Fig. 1 or from (b') to (c') in Fig. 2]. This product is always negative as specified by Eq. 1. It accounts for a closed system where the change of n_i is caused by ζ .

$$\left(\frac{\partial x_i(n_i, \zeta(n_i, Q_x))}{\partial \zeta}\right)_{n_i} \left(\frac{\partial \zeta}{\partial n_i}\right)_{Q_x} < 0$$

which can be written in a more concise form as

$$\left(\frac{\partial x_i}{\partial \zeta}\right)_{n_i^0} \left(\frac{\partial \zeta}{\partial n_i}\right)_{Q_x} < 0 \tag{1}$$

n_i^0 can be used instead of n_i according to theorem 5. Equation 1 signifies that the equilibrium will decrease the amount of change caused by the first term on the right

This mole fraction (d') cannot be reached as theorem 4 states that the new equilibrium concentration cannot be higher than the previous one (a)

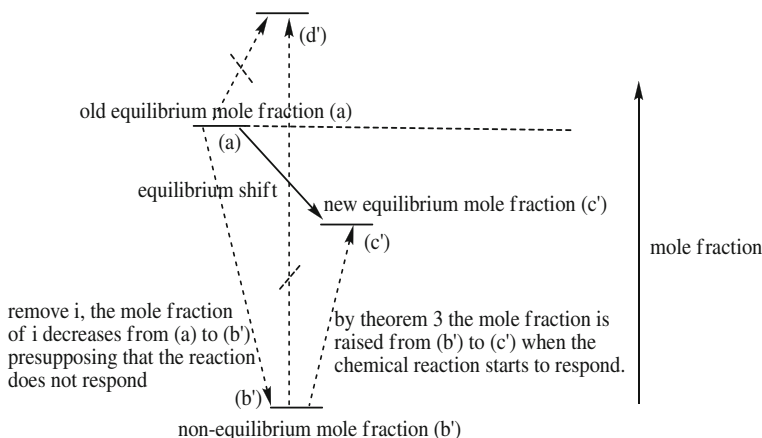


Fig. 2 The equilibrium shifts from (a) to (c') according to theorems 3 and 4. Note that this figure is equivalent to Fig. 1 rotated about a horizontal axis. When species i is removed from an equilibrium system, then x_i changes from (a) to (b'). By theorem 3, x_i would decrease by chemical reaction, from (b') to (c'). The final x_i decreases from (a) to (c'), but never to (d'), which is higher than (a) the initial mole fraction

of Eq. I-42 as is explicitly stated by theorem 3a. Equation 1 can be derived from Eqs. I-33 and I-43. Thus, Eqs. 1 and I-33 are equivalent and are both mathematical representations of theorem 3.

The conclusion of the above analysis is that theorem 3 and 4 can be readily described by Figs. 1 and 2. The equilibrium shift from (a) to (c) obtained by adding species i shown in Fig. 1 can be separated into two interlinked processes (indicated by dotted lines). First that the intensive variable x_i changes from (a) to (b) when the chemical reaction is independent of any outside perturbations (Eq. I-43); second that x_i changes from (b) to (c) when it does respond (theorem 3a or Eq. 1). The equilibrium shift cannot reduce the concentration lower than the initial concentration (theorem 4 or Eq. I-45). i.e. concentration change from (b) to (d) can never happen. Theorem 3b is also represented in Fig. 1. For example if no chemical reaction occurs, in order to make x_i change from (a) to (b), an amount of i is required to be added. If the same change from (a) to (b) is to be maintained under a chemical equilibrium, the addition of more i is subsequently required whether the equilibrium is shifted to reduce or increase the added species. In the above discussion, Eq. 1 is derived from Eqs. I-33 and I-43. Equation I-33 can also be proved by validating Eq. 1. Starting from Eq. I-40 and considering Eqs. I-81 and I-12, we can obtain Eq. 2.

$$\left(\frac{\partial Q_x}{\partial n_i}\right)_{Q_x} = \left(\frac{\partial Q_x}{\partial n_i}\right)_{\zeta, n_j} + \left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_i} \left(\frac{\partial \zeta}{\partial n_i}\right)_{Q_x} = 0 \tag{I-40}$$

$$\left(\frac{\partial Q_x}{\partial n_i}\right)_{\zeta} = Q_x(n_i) \left(\frac{v_i}{n_i} - \frac{\Delta v}{n_T}\right) \tag{I-81}$$

$$\frac{1}{Q_x} \left(\frac{\partial Q_x}{\partial \zeta} \right)_{n_i^0} = \left(\sum_{i=1}^N \frac{v_i^2}{n_i} \right) - \frac{\left(\sum_{i=1}^N v_i \right)^2}{\sum_{i=1}^N n_i} \geq 0 \quad (\text{I-12})$$

Now rearranging Eq. I-40 and then replacing the numerator and denominator by Eq. I-81 and I-12 respectively, we obtain Eq. 2. Note that in Eq. 2 we have used eq I-44 to convert $\left(\frac{\partial Q_x}{\partial n_i} \right)_{\zeta, n_j}$ to $\left(\frac{\partial x_i}{\partial \zeta} \right)_{n_i}$ since they only differ from each other by positive multipliers of x_i and Q_x , respectively.

$$\left(\frac{\partial x_i}{\partial \zeta} \right)_{n_j} = x_i \left(\frac{v_i}{n_i} - \frac{\Delta v}{n_T} \right) \quad (\text{I-44})$$

$$\left(\frac{\partial \zeta}{\partial n_i} \right)_{Q_x} = - \frac{\left(\frac{\partial Q_x}{\partial n_i} \right)_{\zeta, n_j}}{\left(\frac{\partial Q_x}{\partial \zeta} \right)_{n_j}} = - \frac{\frac{v_i}{n_i} - \frac{\Delta v}{n_T}}{\sum_i \frac{v_i^2}{n_i} - \frac{(\sum_i v_i)^2}{n_T}} = - \frac{\frac{1}{x_i} \left(\frac{\partial x_i}{\partial \zeta} \right)_{n_i}}{\frac{1}{Q_x} \left(\frac{\partial Q_x}{\partial \zeta} \right)_{n_j}} = - \frac{1}{k} \left(\frac{\partial x_i}{\partial \zeta} \right)_{n_i}$$

$$\text{where } k = x_i \left[\sum_i \frac{v_i^2}{n_i} - \frac{(\sum_i v_i)^2}{n_T} \right] > 0 \quad (2)$$

Here the denominator k is positive following Eq. I-12. Thus, Eq. 1 is proved from Eq. 2. Equation 3 can also be obtained from Eq. 2, or from I-34 taking Eq. I-12 into account. Eq. I-12 is related to the Schwarz inequality and thus so is theorem 3.

$$\left(\frac{\partial Q_x}{\partial n_i} \right)_{\zeta, n_j} \left(\frac{\partial \zeta}{\partial n_i} \right)_{Q_x} < 0 \quad (3)$$

It is seen from the derivations that Eqs. 1 and 3 are equivalent mathematically and that Eq. 3 is mathematically equivalent to Eq. I-34 in the light of theorem 3.

2.1.2 Correlation between theorem 3 and Eq. I-35

It is now possible to show that Eq. I-35 is consistent with theorem 3. VdP is used below in Eq. 8 which implies that P and V are conjugated intensive and extensive variables. The relationship of the corresponding conjugated variables can be expressed in partial derivative form as shown by Eq. I-41. If x_i in Eq. I-42 is replaced by P , and n_i by V , then the graphical representation Figs. 1 and 2 can be changed to represent Eq. I-41 when V is decreased and increased, respectively.

$$\left(\frac{\partial P}{\partial V}\right)_{S,A} = \left(\frac{\partial P}{\partial V}\right)_{S,\zeta} + \left(\frac{\partial P}{\partial \zeta}\right)_{S,V} \left(\frac{\partial \zeta}{\partial V}\right)_{S,A} \tag{I-41}$$

For an ideal gas system, when V increases, then P will decrease. i.e.

$$\left(\frac{\partial P}{\partial V}\right)_{S,\zeta} < 0 \tag{4}$$

Thus, Eq. I-35 requires $\left(\frac{\partial P}{\partial \zeta}\right)_{S,V}$ and $\left(\frac{\partial \zeta}{\partial V}\right)_{S,A}$ to have the same sign as indicated by Eq. 5.

$$\left(\frac{\partial P}{\partial \zeta}\right)_{S,V} \left(\frac{\partial \zeta}{\partial V}\right)_{S,A} > 0 \tag{5}$$

It can be shown that the first term on the right hand side of Eq. I-41 is negative (Eq. 4). i.e. the pressure decreases as the volume increases if the chemical reaction is frozen. It can be represented by the change from (a) to (b') in Fig. 2 when the system expands. The second term gives the increase in pressure caused by the equilibrium shift specified by Eq. 5 to reduce part of the decrease in the intensive quantity P caused by the first term, which is exactly stated by theorem 3. It can be represented by the change from (b') to (c') in Fig. 2. It is easy to understand from the above explanation why Eqs. 1 and 3 include <0 while Eq. 5 includes >0 and why Eqs. I-33–I-35 have a similar form. This is the reason why it is more logical to use Eqs. I-33–I-35 rather than Eqs. 1, 3, and 5 as the mathematical representation of theorem 3.

Equation 5 above can be derived from Eqs. 4 and I-35. Conversely, Eq. I-35 can also be derived from Eq. 5 as follows. We first define a quantity A in Eq. 6 which represents the negative partial derivative of the internal energy U with respect to ζ at constant entropy S and volume V; or alternatively the Gibbs free energy G at constant T and P; or the Helmholtz free energy (work function) F at constant T and V.

$$A = - \sum_i v_i \mu_i = - \left(\frac{\partial U}{\partial \zeta}\right)_{S,V} = - \left(\frac{\partial G}{\partial \zeta}\right)_{P,T} = - \left(\frac{\partial F}{\partial \zeta}\right)_{T,V} \tag{6}$$

where μ_i represents the chemical potential of species i. Some relevant thermodynamic relationships are given by Eqs. 7–10.

$$dU = TdS - PdV - Ad\zeta \tag{7}$$

$$dG = -SdT + VdP - Ad\zeta \tag{8}$$

$$dF = -SdT - PdV - Ad\zeta \tag{9}$$

$$A = A(S, V, \zeta) \tag{10}$$

From Eq. 10 we can derive Eqs. 11 and 12.

$$dA = \left(\frac{\partial A}{\partial V}\right)_{S,\zeta} dV + \left(\frac{\partial A}{\partial \zeta}\right)_{S,V} d\zeta \quad (11)$$

$$\left(\frac{\partial \zeta}{\partial V}\right)_{S,A} = -\frac{\left(\frac{\partial A}{\partial V}\right)_{S,\zeta}}{\left(\frac{\partial A}{\partial \zeta}\right)_{S,V}} \quad (12)$$

We obtain Eq. 13 from Eq. 7.

$$\left(\frac{\partial P}{\partial \zeta}\right)_{S,V} = \left(\frac{\partial A}{\partial V}\right)_{S,\zeta} \quad (13)$$

By inserting Eq. 13 into Eq. 12, then Eq. 14 is obtained. The final term on the right hand side of Eq. 1-41 is related to Eq. 14.

$$\left(\frac{\partial \zeta}{\partial V}\right)_{S,A} = -\frac{\left(\frac{\partial A}{\partial V}\right)_{S,A}}{\left(\frac{\partial A}{\partial \zeta}\right)_{S,V}} = -\frac{\left(\frac{\partial P}{\partial \zeta}\right)_{S,V}}{\left(\frac{\partial A}{\partial \zeta}\right)_{S,V}} \quad (14)$$

We can prove Eq. 15 from Eqs. 6, 16 and I-30.

$$\left(\frac{\partial A}{\partial \zeta}\right)_{S,V} < 0; \quad \left(\frac{\partial A}{\partial \zeta}\right)_{T,V} < 0; \quad \left(\frac{\partial A}{\partial \zeta}\right)_{T,P} \leq 0 \quad (15)$$

We know that G is a minimum at equilibrium. From Eq. 6 we can obtain Eq. 16.

$$-\left(\frac{\partial A}{\partial \zeta}\right)_{T,P} = \left(\frac{\partial^2 G}{\partial \zeta^2}\right)_{T,P} \geq 0 \quad (16)$$

Thus, Eq. 5 can be proved from Eq. 14 by using Eq. 15, and Eq. 5 is a natural consequence of Eqs. 14 and 16. It should be noted that Figs. 1 and 2 only apply to conjugated variables such as P and V or concentration x_i and amount n_i of the added species i as detailed in Appendix 1.

We have shown that Eqs. 1, 3 and 5 are the mathematical expressions of theorem 3. At the same time we showed that from these equations we can obtain the equivalent Eqs. I-33–I-35. Equations 1 and 3 include <0 but Eq. 5 includes >0 . However, Eqs. I-33, I-34, and I-35 all include -1 so that they are not only more uniform and elegant than their counterparts but they can be directly related to the chemistry expressed in theorem 3.

2.2 Judging the direction of equilibrium shift

An important aspect of equilibrium theory is the ability to predict the direction of any equilibrium shift. A variety of mathematical approaches are used in this section to

determine the shift. It will be shown here that theorems 1–3 can be consistently used to establish the direction of equilibrium shift for an ideal gas system at constant T and P.

2.2.1 Relationship between Eq. 1 and theorem 3

Equation 1 which is correlated with theorem 3 can be used to obtain the direction of the shift in the equilibrium. When species i is added to the system, the extensive quantity n_i is increased. The first term, on the right hand side of Eq. I-42, namely Eq. I-43 shows that x_i will increase before any equilibrium shift occurs. It is necessary to reduce the intensive quantity x_i according to theorem 3a before a new equilibrium can be formed. After the addition, the system becomes closed. If $\left(\frac{\partial x_i}{\partial \zeta}\right)_{n_i} > 0$, then ζ needs to decrease in order to reduce x_i , which is a necessary consequence of theorem 3a that requires any equilibrium shift to decrease the change in the intensive quantity x_i . As a consequence, the addition of species i will result in a decrease in ζ . Thus $\left(\frac{\partial \zeta}{\partial n_i}\right)_{K_x} < 0$ or $\left(\frac{\partial \zeta}{\partial n_i}\right)_{Q_x} < 0$. So, theorem 3 is consistent with Eq. 1 in which the two derivatives have opposite signs. On the other hand, if $\left(\frac{\partial x_i}{\partial \zeta}\right)_{n_i} < 0$, ζ must increase in order to reduce x_i according to theorem 3a. Note that in this case species i is added which means that an increase in n_i gives rise to an increase in ζ , thus $\left(\frac{\partial \zeta}{\partial n_i}\right)_{K_x} > 0$ or $\left(\frac{\partial \zeta}{\partial n_i}\right)_{Q_x} > 0$, conforming with Eq. 1.

2.2.2 Relationships between theorems 1 and 3

From Eq. 2

$$\left(\frac{\partial \zeta}{\partial n_i}\right)_{Q_x} = -\frac{\left(\frac{\partial x_i}{\partial \zeta}\right)_{n_i}}{x_i \frac{1}{Q_x} \left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_j}}$$

we see that Eq. 1 of theorem 3 connects with Eq. I-9 relevant to theorem 1. Equation 3 represents another mathematical expression that can be correlated with theorem 3. It conforms to theorem 1 in judging the direction of equilibrium shift. If $\left(\frac{\partial Q_x}{\partial n_i}\right)_{\zeta, n_j} > 0$, then an increase in n_i causes an increase in Q_x by freezing the chemical reaction. According to theorem 1, the equilibrium will be shifted backwards to reduce the value of Q_x to K_x . Thus an increase in n_i must cause ζ to decrease when the freeze is lifted, resulting in $\left(\frac{\partial \zeta}{\partial n_i}\right)_{K_x} < 0$. Thus, the two derivatives have opposite signs as specified by Eq. 3. Therefore, theorems 1 and 3 are self-consistent. If $\left(\frac{\partial Q_x}{\partial n_i}\right)_{\zeta, n_j} < 0$, then an increase in n_i causes a decrease in Q_x . According to theorem 1, the equilibrium will be shifted forwards to increase the value of Q_x , resulting in $\left(\frac{\partial \zeta}{\partial n_i}\right)_{K_x} > 0$, conforming to Eq. 3. Equation 3 and theorem 1 are therefore also self-consistent.

2.2.3 Relationship between theorems revealed by statement S1

For a systematic theory it is necessary to establish coherent connections between different concepts. Here we take the following statement S1 from [3] and show that it is consistent with theorems 1–4.

S1: The addition at constant T and P of a small amount of reacting species i in an ideal-gas equilibrium mixture will shift the equilibrium to produce more i when two conditions are both satisfied: first that the species i appears on the side of the chemical equation for which the sum of coefficients is the greater and second that the equilibrium mole fraction x_i of species i satisfies Eq. 17.

$$x_i > \frac{v_i}{\Delta v} \quad (17)$$

2.2.3.1 Relationship between S1 and theorems 1 and 3

If the added species i is on the side of the chemical equation for which the sum of coefficients is the greater, then, v_i and Δv will definitely have the same sign. Note that the sign of Δv will be positive or negative, depending on which side of the reaction equation has the greater sum of coefficients. When species i is added ($dn_i > 0$) as a product ($v_i > 0$), and the product i appears on the side of the equation with the greater sum of the coefficients ($\Delta v > 0$), we have $\frac{v_i}{\Delta v} > 0$. Corresponding result can be obtained for reactant. When $x_i < \frac{v_i}{\Delta v} > 0$, from Eq. I-81, then $\left(\frac{\partial Q_x}{\partial n_i}\right)_{\zeta, n_j} > 0$ for $\Delta v > 0$ if i is a product ($v_i > 0$) and $\left(\frac{\partial Q_x}{\partial n_i}\right)_{\zeta, n_j} < 0$ for $\Delta v < 0$ if i is a reactant ($v_i < 0$). Since the equilibrium will restore Q_x to K_x according to theorem 1, the equilibrium will be shifted to decrease the amount of added species i . As i is added continuously, the equilibrium concentration x_i will be increased according to theorem 4. When $x_i > \frac{v_i}{\Delta v} > 0$, then Eq. I-81 requires that $\left(\frac{\partial Q_x}{\partial n_i}\right)_{\zeta, n_j} < 0$ for $\Delta v > 0$, where i is a product and $\left(\frac{\partial Q_x}{\partial n_i}\right)_{\zeta, n_j} > 0$ for $\Delta v < 0$, where i is a reactant. According to theorem 1, the equilibrium will be shifted to increase the amount of added species i . Although the amount of i is increased by the shift, x_i still decreases via the equilibrium shift according to theorem 3. This will be discussed further in Sect. 2.2.3.5. For example, from row (i) to row (ii) in Table 2 when 1 mole of N_2 is added while the equilibrium is frozen, it is shown that x_{N_2} is increased from 0.5000 to 0.6973. When a new equilibrium is reached in row (iii), more N_2 is produced as indicated by S1 since $x_{N_2} = 0.6973 > \frac{v_i}{\Delta v} = \frac{-1}{-2}$ and x_{N_2} is decreased from 0.6973 to 0.6966 though n_{N_2} is increased, conforming to theorem 3 or Eq. 1. If species i is on the side of the chemical equation for which the sum of coefficients is the smaller, then v_i and Δv will possess opposite signs. The condition $x_i > \frac{v_i}{\Delta v} < 0$ will then always be true. From the same analysis, it can be concluded that the equilibrium will be shifted to decrease the amount of i . Thus it is confirmed that S1 is a natural consequence of theorems 1 and 3.

2.2.3.2 Relationship between S1 and theorems 2 and 4

The two conditions in S1 can also be obtained from theorem 2. When $\frac{v_i}{\Delta v} < 0$, it can be shown easily that both effects stated by theorems 2a and 2b shift the equilibrium to the same side of the chemical equation. Both effects result in a decrease in the amount of the added species i , which conforms to the above statement S1.

By contrast however, when $\frac{v_i}{\Delta v} > 0$, the effects stated by theorem 2a and 2b shift the equilibrium in opposite directions. Suppose i is a product. Let us start from the original equilibrium mole fraction of species i when it satisfies the condition specified in Eq. 18 before the product i is added.

$$x_i = \frac{n_i}{n_T} < \frac{v_i}{\Delta v} \quad (18)$$

Equation 18 signifies that $\left| \frac{v_i}{n_i} \right|$ is greater than $\left| \frac{\Delta v}{n_T} \right|$.

$$Q_x(n_i + dn_i) = Q_x(n_i) \frac{\left(1 + \frac{v_i dn_i}{n_j}\right)}{\left(1 + \frac{\Delta v dn_i}{n_T}\right)} \quad (\text{I-79})$$

From Eq. I-79, it can be seen that in this case the effect of theorem 2b is greater than that of theorem 2a and therefore the equilibrium shifts to reduce the amount of added species. As stated by theorem 4 the new equilibrium concentration x_i will increase as species i is added. Thus, theorem 4 ensures that Eq. 19 will eventually become valid as i is added.

$$x_i = \frac{n_i}{n_T} > \frac{v_i}{\Delta v}; \text{ or } \left| \frac{v_i}{n_i} \right| < \left| \frac{\Delta v}{n_T} \right| \quad (19)$$

Equations I-79 and 19 signify that the effect of theorem 2a is greater than that of 2b at this time and so, for example, the equilibrium will shift to the right to provide more of the added product since i is on the side with the greater sum of coefficients. A similar result can be obtained for reactant. From the old equilibrium (i) to the new equilibrium (iii) in Table 2, x_{N_2} increases from 0.5000 to 0.6966 even though the volume V of the system is expanded by theorem 2a thus conforming with theorem 4. In fact Eq. 19 is equivalent to Eq. 17. Thus, S1 is a natural consequence of theorems 2 and 4.

2.2.3.3. The fundamental nature of theorem 2

Theorem 2 is an important part of our chemical equilibrium approach but it also has significant consequences when considered in isolation. From the above discussion, it is easy to understand that the direction of equilibrium shift predicted by theorems 2a or 2b is fixed whatever the value of x_i . However it can be noted that the equilibrium shift in S1 changes direction at the condition specified by Eq. 20.

$$x_i = \frac{v_i}{\Delta v} > 0 \quad (20)$$

Thus, the effects stated in theorem 2, which are extracted from the application of mathematical techniques, are more fundamental and go beyond the propositions considered in statement S1.

2.2.3.4 Relationship between S1 and the maximum fractional conversion ratio of reactant

Another point deserves to be mentioned here. When reactant i ($v_i < 0$) is added and the reactant side of the equation has the greater sum of the coefficients ($\Delta v < 0$), then according to the above discussion, the fractional conversion of another reactant j , for an ideal gas system at any given temperature and pressure, has a maximum when Eq. 20 is satisfied [4]. Note that in this case both the numerator v_i and the denominator Δv are negative, so x_i will be positive. Thus, before Eq. 20 is satisfied, x_i is small and the effect stated by theorem 2b dominates. Under these conditions, the equilibrium will shift to reduce both reactants i and j , thus increasing the fractional conversion of j . When Eq. 20 is satisfied, the fractional conversion of j reaches a maximum. It is easy to prove mathematically that Eq. 20 is equivalent to Eq. I-53 from theorem 6. When Eq. 17 is finally satisfied for reactant i , the effect stated by 2a dominates and the equilibrium will shift to produce more i and j . Thus, the conversion ratio of reactant j will decrease. When the added species is a product, theorems 4 and 6 becomes relevant and this will be discussed below in Sects. 2.3.2 and 2.3.3.

2.2.3.5 Relationship between S1 and theorems 2 and 3

Even for the case where the equilibrium of the reaction shifts to produce more of the added species i as stated in S1, the equilibrium shift initiates a process from (b) to (c) in Fig. 1 to reduce the value of the intensive variable x_i as specified by theorem 3 or Eq. 1. This is because the equilibrium shifts to the side with the greater sum of coefficients, thus increasing n_T . The increase in n_T which dilutes the system will have a greater effect than that created by increasing n_i , i.e. the effect specified by theorem 2a is greater than that specified by 2b in such cases. The relevance of theorem 2 in this case can be detailed mathematically. As mentioned above, Eq. I-44 is complementary to Eq. I-82 in that they only differ from each other by a positive factor. A similar relationship is found between Eqs. 21 and I-62 or I-79.

$$x_i(n_i + dn_i) = x_i(n_i) \frac{\left(1 + \frac{v_i dn_i}{n_j}\right)}{\left(1 + \frac{\Delta v dn_i}{n_T}\right)} \quad (21)$$

Thirdly, Eq. 1 is complementary to Eq. 3 as discussed in Sects. 2.2.1 and 2.2.2. Thus, theorem 2 can be applied similarly in this case. When $x_i > \frac{v_i}{\Delta v} < 0$, then according to both theorems 2a and 2b, the reaction will be shifted to reduce x_i as shown by Proofs P5 and P6 in Part I of this work. When $\frac{v_i}{\Delta v} > 0$, the effects of theorems 2a and 2b will

shift the reaction in different directions and the effect of theorem 2b is dominant when $x_i < \frac{v_i}{\Delta v} > 0$. Thus, the decrease in n_i reduces x_i . When $x_i > \frac{v_i}{\Delta v} > 0$, the effect of theorem 2a is dominant. Thus, the increase in n_T reduces x_i . Two other mathematical expressions of theorem 3 [5,6], namely Eqs. 22 and 23 are discussed below.

2.2.4 Judging the direction of equilibrium shift by Eq. 22

Theorem 3 can also be expressed mathematically in terms of the specific intensive variable x_i and its extensive variable n_i , as Eq. 22.

$$\left(\frac{dx_i}{dt}\right)_{K_x} \delta n_i < 0 \tag{22}$$

The significance of Eq. 22 is detailed below. When species i is added then $\delta n_i > 0$. x_i will increase [from (a) to (b) as in Fig. 1] when the reaction extent does not change. However, if the reaction starts to respond, x_i will decrease according to theorem 3 [from (b) to (c) as in Fig. 1], resulting in $\left(\frac{dx_i}{dt}\right)_{K_x} < 0$ thus conforming with Eq. 22 for the chemical reaction; Note the subtle difference between theorems 3 and 4 in that the equilibrium is shifted to increase the equilibrium value of x_i [from (a) to (c) in Fig. 1] according to theorem 4. Alternatively when i is removed from the system ($\delta n_i < 0$), x_i will decrease [from (a) to (b') in Fig. 2] when the reaction does not respond. According to Eq. 22 $\left(\frac{dx_i}{dt}\right)_{K_x} > 0$ when the chemical reaction starts to respond, resulting in an increase in x_i [from (b') to (c') in Fig. 2] thus confirming theorem 3.

2.2.5 Judging the direction of equilibrium shift by Eq. 23

Theorem 3 also conforms with the thermodynamic principle that a process with $\Delta G < 0$ is spontaneous for a system at constant T and P . When the specific intensive variable $\left(\frac{\partial G}{\partial \zeta}\right)_{T,P,n_i^0}$ and its extensive variable $\left(\frac{d\zeta}{dt}\right)_{K_x}$ are considered, theorem 3 can be expressed mathematically by Eq. 23.

$$\left(\frac{\partial G}{\partial \zeta}\right)_{T,P,n_i^0} \left(\frac{d\zeta}{dt}\right)_{K_x} \leq 0 \tag{23}$$

Equation 23 can be easily proved. Since

$$G = G\left(T, P, n_i^0, \zeta\right) \tag{24}$$

For a spontaneous process, then

$$dG = \left(\frac{\partial G}{\partial n_i^0}\right)_{T,P,\zeta} dn_i^0 + \left(\frac{\partial G}{\partial \zeta}\right)_{T,P,n_i^0} d\zeta \leq 0 \tag{25}$$

The equilibrium shift process is a closed system and therefore the total number of moles will not change with time, thus, $\left(\frac{\partial n_i^0}{\partial t}\right)_{T,P,G} = 0$, so Eq. 26 can be derived from Eq. 25.

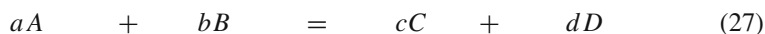
$$\left(\frac{dG}{dt}\right)_{T,P,n_i^0} = \left(\frac{\partial G}{\partial \zeta}\right)_{T,P,n_i^0} \left(\frac{d\zeta}{dt}\right)_{T,P,G,n_i^0} \leq 0 \quad (26)$$

It can readily be seen that Eq. 26 is the same as Eq. 23. G is a minimum at equilibrium. i.e. spontaneously always proceeds to reduce G till a minimum is reached. So, when $\left(\frac{\partial G}{\partial \zeta}\right)_{T,P,n_i^0} < 0$, then $\frac{d\zeta}{dt} > 0$ according to Eq. 26 so that G is reduced, resulting in a forward reaction; Conversely when $\left(\frac{\partial G}{\partial \zeta}\right)_{T,P,n_i^0} > 0$, then $\frac{d\zeta}{dt} < 0$ according to Eq. 23, resulting in a backwards reaction so that G is again reduced.

2.3 Connections revealed by the theorems

2.3.1 Conditions for maximizing the fractional conversion ratio of a reactant

We will show an example for which theorem 5 is particularly important. The maximum fractional conversion condition for reactant B with Eq. 27 is shown in [4] to be when the initial mole ratio satisfies Eq. 28.



$$\zeta = 0 \quad n_A(0) = n_A^0 = R \quad n_B(0) = n_B^0 = 1 \quad n_C(0) = 0 \quad n_D(0) = 0 \quad (i)$$

$$\zeta = \zeta(t) \quad n_A(t) = n_A^0 - a\zeta \quad n_B(t) = n_B^0 - b\zeta \quad n_C(t) = n_C^0 + c\zeta \quad n_D(t) = n_D^0 + d\zeta \quad (ii)$$

Rows (i) and (ii) of Eq. 27 indicate the number of moles at time 0 and time t respectively.

$$R = \frac{a}{b - c - d} \quad \text{where } a + b > c + d \quad (28)$$

R is the initial amount of A in Eq. 27. This condition is just a different side of the same coin expressed by Eq. 20 in Sect. 2.2.3.3 which allows the extreme value of the reaction extent to be obtained. The theoretical basis of this has previously been given in Sect. 2.2.3.4. The difference is that Eq. 20 is expressed in terms of equilibrium concentration while Eq. 28 is expressed in term of n_i^0 or R. We can show that Eqs. 28 and 20 are equivalent. Inserting Eq. I-5 into Eq. 20, we obtain Eq. 29.

$$\frac{n_i^0 + v_i \zeta}{\left(\sum_j n_j^0\right) + \Delta v \zeta} = \frac{v_i}{\Delta v}; \quad \text{or} \quad \frac{n_i^0}{\left(\sum_j n_j^0\right)} = \frac{v_i}{\Delta v} \quad (29)$$

Equations 30 and 31 can be obtained from Eq. 29

$$n_i^0 \left(v_i + \sum_{j \neq i} v_j \right) - v_i \left(n_i^0 + \sum_{j \neq i} n_j^0 \right) = n_i^0 \sum_{j \neq i} v_j - v_i \sum_{j \neq i} n_j^0 = 0 \quad (30)$$

$$\frac{n_i^0}{\sum_{j \neq i} n_j^0} = \frac{v_i}{\sum_{j \neq i} v_j} \quad (31)$$

Equation 31 is just a general form of Eq. 28, i.e. Eq. 20 is equivalent to Eq. 31 which takes into account that the initial numbers of moles of products are non-zero as shown in Eq. 27 (row ii). The fact that Eqs. 20 and 28 are equivalent is a direct consequence of theorem 5. A proof of theorem 1 in terms of n_i^0 has been given as Proof P3 in part I of this work.

2.3.2 Conditions for maximizing the mole fraction of a product

We consider the specific reaction given in Eq. 32



In [4] it is proved that the optimum condition for maximizing the mole fraction of the product C in this reaction is given by Eq. 33.

$$\frac{n_A^0}{n_B^0} = \frac{a}{b} \quad (33)$$

The conditions for the maximum equilibrium concentration of product in theorem 6 have been derived in part I of this work more generally than in [4]. From theorem 5, the optimum condition given by Eq. 33 [4] which involves n_r^0 of the reactant is equivalent to that given in Eq. I-53 which involves n_j together with non-zero values of $n_{p'}$ for products. In fact, Eq. I-53 is more general than the literature formula [4] since it allows for the presence of products. The conditions at time t in row (ii) of the reaction given by Eq. 27 can be evolved from the conditions at t = 0 in (i). So, by theorem 5, the condition for t = 0 is equivalent to that at time t. Every condition for equilibrium properties expressed in n_i can be converted to an equivalent condition expressed in n_i^0 according to theorem 5. For example, by inserting Eq. I-2 into Eq. I-20 or I-53, we obtain Eq. 34 which is a general form of Eq. 33.

$$\frac{n_j}{n_k} = \frac{n_j^0 + v_j \zeta}{n_k^0 + v_k \zeta} = \frac{v_j}{v_k} \Rightarrow \frac{n_i^0}{n_j^0} = \frac{v_i}{v_j} \quad (34)$$

Previous discussion in the literature [4] is based upon a specific equation such as Eq. 32 when $\zeta = 0$ as shown in Eq. 27, with initial conditions given at row (i), where no products exist when the reaction extent is 0. We, however, started more generally from Eq. I-1 and the Lagrange multiple constant method, with initial conditions after

time t given by row (ii) as well as that at time 0 by row (i) but allowing n_C^0 and n_D^0 to be non-zero.

2.3.3 Connection between theorems 4 and 6

We now show that theorem 4 is a specific case of theorem 6. When adding product p , x_p will increase according to theorem 4. So, the product p should not be included in Eq. I-53 since no maximum value of x_p can be reached as more p is added. We will show that the general Lagrange multiple constant method in Proof P10 is also valid for this situation. We now show that the general Lagrange multiple constant method can also be used to derive Eq. I-45. However, we first need to establish how Eq. I-57 (or I-56 which differs only by the sub-index) is obtained via the Lagrange multiple constant method. Equations I-39 and I-40 can be combined as (I-39) + λ (I-40), to give Eq. 35.

$$\left(\frac{\partial x_p}{\partial n_k^0}\right)_{K_x} + \lambda \left(\frac{\partial Q_x}{\partial n_k^0}\right)_{K_x} = \left[\left(\frac{\partial x_p}{\partial n_k^0}\right)_{\zeta} + \lambda \left(\frac{\partial Q_x}{\partial n_k^0}\right)_{\zeta} \right] + \left[\left(\frac{\partial x_p}{\partial \zeta}\right)_{n_j^0} + \lambda \left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_j^0} \right] \left(\frac{\partial \zeta}{\partial n_k^0}\right)_{K_x} \quad (35)$$

where λ is a constant which is specified from Eq. 36.

$$\left[\left(\frac{\partial x_p}{\partial \zeta}\right)_{n_j^0} + \lambda \left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_j^0} \right] = 0 \quad (36)$$

which on rearrangement gives Eq. 37

$$\lambda = - \frac{\left(\frac{\partial x_p}{\partial \zeta}\right)_{n_j^0}}{\left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_j^0}} \quad (37)$$

When Eq. 37 is inserted into Eq. 35, the last term on the right hand side of Eq. 35 vanishes. Setting the first term on the right hand side of Eq. 35 to 0, we then obtain Eq. I-57, which represents the condition for the Lagrange conditional maximum.

$$\left(\frac{\partial x_p}{\partial n_k^0}\right)_{\zeta} + \lambda \left(\frac{\partial Q_x}{\partial n_k^0}\right)_{\zeta} = 0 \quad (\text{I-57})$$

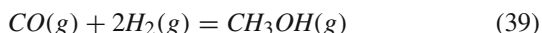
Inserting Eq. 37 into Eq. I-57 and letting $k = p$, we obtain Eq. 38.

$$\left(\frac{\partial x_p}{\partial n_p^0}\right)_\zeta - \left(\frac{\partial Q_x}{\partial n_p^0}\right)_\zeta \frac{\left(\frac{\partial x_p}{\partial \zeta}\right)_{n_j^0}}{\left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_j^0}} = \left(\frac{\partial x_p}{\partial n_p^0}\right)_\zeta + \left(\frac{\partial x_p}{\partial \zeta}\right)_{n_j^0} \left(\frac{\partial \zeta}{\partial n_p^0}\right)_{K_x} \quad (38)$$

Equation 38 is equivalent to Eq. I-42 or I-45. So, theorem 4 represents a special case of theorem 6. Thus, when product p is involved, theorem 4 applies and it implies that adding product p will increase x_p . When p is in large excess, x_p approaches 1. So, in theorem 6, p has been excluded.

2.4 Effects of scale upon chemical equilibrium

An application of the theorems is given to show that the rules or patterns for small scale experiments in the laboratory might be different from those for large scale industrial applications. Let us consider the simple reaction for the formation of methanol given in Eq. 39.



example 1	1	m	0
	$1 - \zeta$	$m - 2\zeta$	ζ
example 2	R	1	0
	$R - \xi$	$1 - 2\xi$	ξ

1, m, and R in Eq. 39 are the initial numbers of moles. ζ and ξ are the reaction extents for the two examples. Suppose the equilibrium constant K_x is 2.97 at a specific T and P. Then for example 1

$$K_x = \frac{\zeta(1 + m - 2\zeta)^2}{(1 - \zeta)(m - 2\zeta)^2} = 2.97 \quad (40)$$

And for example 2

$$K_x = \frac{\xi(1 + R - 2\xi)^2}{(R - \xi)(1 - 2\xi)^2} = 2.97 \quad (41)$$

In example 1, we now assume that the initial mole ratio m varies between 0.5 and 5.0 while in example 2, it varies between 2.0 and 0.2. The resulting equilibrium quantities calculated using Eqs. 40 and 41 are given in Table 1.

The reaction extent ξ has a maximum value at $x_{CO} = 0.5$ predicted from Eq. 20 or $R = 1$ predicted from Eq. 31 for example 2 (Table 1). The conclusions predicted from Eqs. 20 and 31 are the same because of theorem 5. While for example 1, the

maximum value can be theoretically achieved at $x_{\text{H}_2} = 1$ or $m = \infty$ from Eqs. 20 and 31, respectively. But these conditions cannot pertain. Thus, ζ has no maximum value. Note that x_{CO} increases when R is increased from 0.2 through 1 although the reaction will reduce the amount of CO as predicted by Eq. 18. The result conforms to theorem 4.

Let $m = 0.5$ in example 1. Then scale up by a factor of 2 such that initial numbers of moles for CO and H_2 are 2 and 1, respectively, which is equivalent to example 2 when $R = 2$. The calculated equilibrium concentrations x_i for the two examples are identical as shown in Table 1. When the concentrations in example 1 are scaled down m times, the initial amount of reactants becomes $1/m$ and 1 and the reaction extent is similarly scaled down as indicated by Eq. 42.

$$\xi = \frac{\zeta}{m} \quad (42)$$

Also, the first two columns for example 1 will become equivalent to the third and fourth columns for example 2. However, for the reaction extent, example 2 shows a maximum while example 1 does not, despite the fact that the two examples only differ from each other by a multiplication factor. This can be explained as follows:

From Eqs. 2, I-12, and I-82, we can generate Eq. 43.

$$\left(\frac{\partial \zeta}{\partial n_{\text{H}_2}^0}\right)_{K_x, n_{\text{CO}}} = \left(\frac{\partial \zeta}{\partial m}\right)_{K_x, n_{\text{CO}}} = -\frac{\left(\frac{\partial Q_x}{\partial n_{\text{H}_2}^0}\right)_{\zeta, n_{\text{CO}}^0}}{\left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_{\text{CO}}^0}} = \frac{n_{\text{H}_2}^0 \sum_{i \neq \text{H}_2} v_i - v_{\text{H}_2} \sum_{i \neq \text{H}_2} n_i^0}{n_{\text{H}_2}^0 \left[\sum_i n_i \sum_i \frac{v_i^2}{n_i} - \left(\sum_i v_i\right)^2 \right]} \quad (43)$$

$\sum_{i \neq \text{H}_2} v_i = 0$, $\sum_{i \neq \text{H}_2} n_i^0 = n_{\text{CO}}^0 = 1$, $n_{\text{H}_2}^0 = m$, and $v_{\text{H}_2} = -2$. So, the numerator of Eq. 43 is positive and constant but $\left(\frac{\partial \zeta}{\partial m}\right)_{K_x, n_{\text{CO}}}$ is variable because the denominator of Eq. 43 is variable.

Table 1 Initial mole ratio, equilibrium reaction extents and equilibrium concentration

Example 1		Example 2		Equilibrium concentration		
m	ζ	R	ξ	$x_{\text{CH}_3\text{OH}}$	x_{H_2}	x_{CO}
0.500	0.117	2.000	0.234	0.092	0.210	0.698
0.670	0.163	1.500	0.244	0.121	0.255	0.624
1.000	0.250	1.000	0.250	0.167	0.333	0.500
2.000	0.450	0.500	0.225	0.214	0.524	0.262
3.000	0.560	0.333	0.185	0.194	0.651	0.151
4.000	0.620	0.250	0.154	0.164	0.735	0.102
5.000	0.650	0.200	0.130	0.138	0.787	0.074

We differentiate Eq. 42 with respect to m under equilibrium conditions to obtain Eq. 44.

$$\left(\frac{\partial \xi}{\partial m}\right)_{K_x} = \left(\frac{\partial \frac{\zeta}{m}}{\partial m}\right)_{K_x} = -\frac{\left(\frac{\partial \zeta}{\partial m}\right)_{K_x} m - \zeta}{m^2} = \frac{\left(\frac{\partial \zeta}{\partial m}\right)_{K_x} - \frac{\zeta}{m}}{m} \quad (44)$$

Although ζ has no maximum value with respect to m , it has a maximum value when the system is reduced by a factor of m . That is when $\left(\frac{\partial \xi}{\partial m}\right)_{K_x}$ in Eq. 44 has a critical point, or when $\left(\frac{\partial \zeta}{\partial m}\right)_{K_x}$ in Eq. 44 changes from $>=$ to $<=$ $\frac{\zeta}{m}$.

This example shows that mathematics can be used to investigate different patterns in a scaled reaction.

2.5 The problems inherent in the traditional formulation of the Le Chatelier Principle

A system can be described with many pairs of conjugated variables such as x_i and n_i ; T and q , the amount of heat absorbed; or P and V . If no equilibrium exists, then when applying an action such as increasing the intensive variable x_i , T or P , then the system will respond by generating a reaction and increasing the relevant conjugated extensive variable n_i , q or decreasing V . Conversely if the applied action is the change in the extensive variable n_i , q or V , the reaction will be the change in the intensive variable x_i , T or P . The traditional Le Chatelier Principle is often expressed by one or other of the two different statements S2 and S3.

S2: An equilibrium shift is always counteracts the action.

S3: An equilibrium shift is always counteracts the reaction.

However it is obvious that S2 and S3 cannot be correct at the same time. When S2 is correct then S3 must be wrong and vice versa. For example consider the equilibrium of liquid and gaseous water. If we define increasing P or decreasing T as the action, then it can be shown that S2 gives the correct prediction, but that S3 does not. S3 predicts that the equilibrium will shift by converting more liquid water to gaseous water to counteract the decrease in V or increase in q , thus decreasing the heat released to the environment. But this is wrong since increasing P or decreasing T should shift the equilibrium to convert more gaseous water to liquid water. Thus S3 is wrong although S2 is correct in this case. Conversely if we define decreasing V or q as the action, then S3 provides the correct result but S2 does not as it predicts that the equilibrium will counteract the decrease in V or q by converting more liquid water to gaseous water. But in reality decreasing V or q will result in more gaseous water being converted to liquid water by an equilibrium shift. Thus in this instance, S2 is wrong while S3 is correct.

However, if we use theorem 3 and note that x_i , T or P are intensive and n_i , q or V are extensive variables, it is easy to show that the correct predictions are obtained for both the above cases. Indeed we have already shown that Eq. 1 requires a reaction to reduce x_i [from (b) to (c) in Fig. 1] after i is added, independent of whether the

Table 2 Calculations from the Haber process (Eq. 45), using Eqs. 46–51

	R	ζ	n_{N_2}	n_{H_2}	n_{NH_3}	n_T	x_{N_2}	x_{H_2}	x_{NH_3}
(i)	1	0.2330	0.7670	0.3409	0.4661	1.5340	0.5000	0.1962	0.3038
(ii)	2	0.2330	1.7670	0.3049	0.4661	2.5340	0.6973	0.1182	0.1839
(iii)	2	0.2284	1.7716	0.3147	0.4569	2.5432	0.6966	0.1237	0.1797

(i): Original equilibrium state; (ii): 1 mol of N_2 is added to equilibrium state (i) while $\Delta\zeta = 0$; (iii): new equilibrium state where $\Delta\zeta < 0$

chemical equilibrium is shifted to produce or to consume more of the added species (Section 2.2.3.5). The predication obtained from Eq. 1 is consistent with theorem 3 when n_i and x_i are involved. Thus Eq. 1 and theorem 3 are generally applicable while S2 and S3 are not.

3 Conclusions

It is paramount that a theoretical system needs to be coherent and extensive [7–10]. Through the innovative application of mathematical techniques, the connections between the theorems introduced in Part I of this work are discussed in detail. Graphical representations (Figs. 1, 2) of theorems 3 and 4 are presented consistent with the rigorous mathematical derivations. Based on a solid mathematical background, it is shown that the equilibrium will always shift to reduce x_i in a closed system following the addition of i thus according to theorem 3 following the process from (b) to (c) in Fig. 1. However, according to theorem 4, the equilibrium shifts to increase x_i following the process from (a) to (c) in Fig. 1 when n_i is increased in an open system. In this process as species i is added, the equilibrium might shift to increase x_j ($j \neq i$) as shown in Appendix 1. It has been shown that the conditions to obtain the maximum mole fraction of a target product and the maximum conversion ratio of reactant are connected mathematically. A variety of mathematical approaches are established to judge the direction of equilibrium shift. It is demonstrated that it is useful to express the equilibrium properties for a closed system either in terms of initial mole numbers or by equilibrium concentrations x_i and that these are essentially equivalent. Different patterns in a scaled reaction are also investigated by the application of the theorems. Through the applications, it has been shown that the theorems are connected as a coherent system.

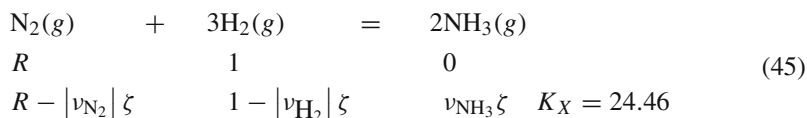
Great effort has been paid in chemistry education to avoid sophisticated mathematical treatments [11–13]. Contrary to the prevalent beliefs, we reckoned that concepts derived from mathematical method can only be fully explained by evoking the relevant mathematical reasoning [14, 15]. The innovations based on original thought should be valued much more than the experimental reports based on advanced apparatus. It has long been realized that the image of chemistry (the image of learning by rote and superficial explanation) needs to be changed by reform in chemical education [16, 17]. It can be argued that chemistry is not a laboratory science [18, 19] and therefore that one way to reform chemical education is to introduce more mathematical logic to reflect modern achievements of chemistry. The material introduced here is consistent with that aim and is suitable for use in mathematical course for chemistry students to show

the capability of mathematical techniques to solve chemical problems. It can also be used independently for upper-division undergraduate or graduate as an advanced course to enhance the students' theoretical basis of equilibrium theory.

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Appendix 1: Non-conjugated variables: the Haber process

It is interesting to note that Figs. 1 and 2 only apply to conjugated variables such as n_i and x_i . However in this Appendix we consider what happens when non-conjugated variables such as n_T the total amount of moles in the system and x_j the concentration of one of the species are considered together. Consider the Haber process to form ammonia from dinitrogen and dihydrogen.



$$Q_x = \frac{x_{\text{NH}_3}^2}{x_{\text{H}_2}^2 x_{\text{N}_2}} \quad (46)$$

$$x_{\text{NH}_3} = \frac{n_{\text{NH}_3}}{n_T} = \frac{\nu_{\text{NH}_3} \zeta}{n_T} \quad (47)$$

$$x_{\text{N}_2} = \frac{n_{\text{N}_2}}{n_T} = \frac{R - |\nu_{\text{N}_2}| \zeta}{n_T} \quad (48)$$

$$x_{\text{H}_2} = \frac{n_{\text{H}_2}}{n_T} = \frac{1 - |\nu_{\text{H}_2}| \zeta}{n_T} \quad (49)$$

$$\begin{aligned} n_T &= n_{\text{N}_2} + n_{\text{H}_2} + n_{\text{NH}_3} = (R - |\nu_{\text{N}_2}| \zeta) + (1 - |\nu_{\text{H}_2}| \zeta) + \nu_{\text{NH}_3} \zeta \\ &= 1 + R + (\nu_{\text{NH}_3} - |\nu_{\text{H}_2}| - |\nu_{\text{N}_2}|) \zeta = 1 + R + \Delta \nu \zeta \end{aligned} \quad (50)$$

$$\Delta \nu = 2 - 3 - 1 = -2 \quad (51)$$

Table 2 lists the results calculated from Eq. 45 using Eqs. 46–51 where R takes the values of 1 and 2.

When 1 more mole of N_2 is added to equilibrium state (i), x_{N_2} increases from 0.5000 to 0.6973 as predicted by Eq. I-43 when ζ remains unchanged at 0.2330. The state of the system goes from (i) to (ii). When the reaction starts to respond, the equilibrium shifts backwards from $\zeta = 0.2330$ to $\zeta = 0.2284$. x_{N_2} decreases from 0.6973 to 0.6966, conforming to theorem 3. The state of the system goes from (ii) to (iii). From (i) to (iii), the equilibrium x_{N_2} increases from 0.5000 to 0.6966, conforming to theorem 4. While for H_2 , x_{H_2} decreases from 0.1962 to 0.1182 for (i) to (ii) because of the addition of N_2 , and increases from 0.1182 to 0.1237 for (ii) to (iii). The backward reaction decreases x_{N_2} but increases x_{H_2} .

The data can be analyzed from another angle. The effect on H_2 of adding 1 more mole of N_2 to (i) is equivalent to that of adding 1 more mole of unreactive (inert) species. x_{H_2} will therefore decrease following the dilution from (i) to (ii). By theorem 2a, the reaction will then go backwards from (ii) to (iii). According to theorem 2a or 3, the equilibrium shift will reduce the dilution. Thus, x_{H_2} increases from (ii) to (iii). In order for the backward reaction to reduce x_{H_2} , Eq. 17 must be satisfied for H_2 . But this is impossible since it requires $x_{H_2} > (-3)/(-2)$. This case can be analyzed in a manner similar to that given in Sect. 2.2.3.5. Strictly speaking, the above analysis is only applicable for infinitesimal changes. If H_2 is added instead of N_2 , the equilibrium will shift forward to consume the reactants since the effect from theorem 2b becomes dominant. The same analysis applies to section 2.4.

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