

A mathematical approach to chemical equilibrium theory for gaseous systems—I: theory

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Abstract Equilibrium theory occupies an important position in chemistry and it is traditionally based on thermodynamics. A novel mathematical approach to chemical equilibrium theory for gaseous systems at constant temperature and pressure is developed. Six theorems are presented logically which illustrate the power of mathematics to explain chemical observations and these are combined logically to create a coherent system. This mathematical treatment provides more insight into chemical equilibrium and creates more tools that can be used to investigate complex situations. Although some of the issues covered have previously been given in the literature, new mathematical representations are provided. Compared to traditional treatments, the new approach relies on straightforward mathematics and less on thermodynamics, thus, giving a new and complementary perspective on equilibrium theory. It provides a new theoretical basis for a thorough and deep presentation of traditional chemical equilibrium. This work demonstrates that new research in a traditional field such as equilibrium theory, generally thought to have been completed many years ago, can still offer new insights and that more efficient ways to present the contents can be established. The work presented here can be considered appropriate as part of a mathematical chemistry course at University level.

Keywords Systematics · Traditional fields · Schwarz inequality · Chemical equilibrium theory · Chemical education

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1 Introduction

Since Newton's time, mathematical reasoning has been valued for revealing much in the natural sciences. The direct result of this attitude is that traditional theories, such as classical mechanics, thermodynamics, statistical physics, and quantum mechanics, etc., are established among the magnificent achievements of mankind. A common feature of the classical theories is that an all-embracing coherent system is established to provide insight on a variety of connected phenomena. Among these amazing insights were the fact that many phenomena, apparently different at first sight, were found to have common features. [1] To establish theoretical systems using mathematics is still valued greatly in today's scientific activity.

Chemical equilibrium theory, which is very important in chemistry, is based on thermodynamics [2–4]. However, this thermodynamic presentation does not automatically provide enough mathematical tools that are required to investigate complicated cases, especially for gaseous systems at constant temperature T and pressure P which are often more complex than liquid systems. This problem is emphasized in a survey conducted by Cheung [5] which shows that the traditional training of chemists is often not sufficiently focused on the treatment of complex equilibrium systems. All the problems described by Cheung involve ideal gas systems at constant T and P . The main conclusion from his survey is that these difficulties are caused not only because the concepts of chemical equilibrium are abstract but also because the presentation of the theory is inadequate. Thus, it is clearly beneficial to develop a more elaborate theoretical system for ideal gas systems at constant T and P .

When mathematical techniques are introduced to support a theory, more insights can often be readily established. Through a novel mathematical approach, we have systemized chemical equilibrium with six theorems that are less reliant on thermodynamics and thus established a new theoretical system from a different perspective. There have been very few attempts in the literature to set up a system for equilibrium theorem mainly from mathematics. The mathematical treatments in the new approach enabled us to provide more insight into and deeper understanding of chemical equilibrium particularly in complex circumstance. The new approach not only provides a new variety of treatment of equilibrium but also provides varieties of mathematical tools to deal with complicated cases. The theorems are coherent and useful for ideal gas systems at constant T and P . While some of the theorems [6–8] have been taken for granted over the years, we develop new ways of considering them as an interconnected set and provide rigorous proofs. One of the prominent features of this work is that it makes use of the Schwarz inequality which we have initially used to provide simple proofs for basic equations and then subsequently expanded to establish the complete coherent system. To the best of our knowledge, the Schwarz inequality has not been used previously in this way. The whole system relies on straightforward mathematics and less on thermodynamics. It provides a new theoretical basis for a thorough and deep presentation of traditional chemical equilibrium.

2 Theorems and proofs

In part I, we first introduce six theorems, which provide a coherent mathematical description of chemical equilibrium, together with their proofs. The six theorems form a system that is most suitable to treat gaseous systems at constant T and P. In a subsequent paper, designated here part II [9], we show how the theorems are connected, and by their application establish the integrated nature of the system. Suitable examples are provided there to elucidate the six somewhat abstract theorems. As an introduction, we first introduce the parameters used and the basic relationships between them denoted in Eqs. 1–6. In a chemical reaction, the reaction quotient, defined in fraction of moles, Q_x^1 , is defined by Eq. 1.

$$Q_x = \prod_{i=1}^N x_i^{v_i} = \prod_{i=1}^N \left(\frac{n_i}{n_T}\right)^{v_i} = \frac{\prod_{i=1}^N n_i^{v_i}}{n_T^{\Delta v}} = \frac{N_x}{D_x} \tag{1}$$

where N_x represents the numerator, $\prod_{i=1}^N n_i^{v_i}$, and D_x the denominator, $n_T^{\Delta v}$. N is the total number of species; i represents a species in a reacting system; n_i is the number of moles of species i (defined in Eq. 2 below); v_i is the coefficient of species i in the relevant balanced chemical equation, being positive when i is a product and negative when it is a reactant. n_T is the sum of the number of moles (defined in Eq. 3) and Δv is the sum of all the coefficients v_i in the balanced chemical equation (defined in Eq. 4). p and r in Eq. 4 represent product and reactant respectively. x_i is the mole fraction for species i (defined in Eq. 5). n_i^0 is the initial number of moles of species i and ζ is the reaction extent.

$$n_i = n_i^0 + \zeta v_i \tag{2}$$

$$n_T = \sum_{i=1}^N n_i = \sum_{i=1}^N (n_i^0 + \zeta v_i) = \left(\sum_{i=1}^N n_i^0\right) + \zeta \sum_{i=1}^N v_i = \left(\sum_{i=1}^N n_i^0\right) + \Delta v \zeta \tag{3}$$

$$\Delta v = \sum_{i=1}^N v_i = \left(\sum_p v_p\right) - \sum_r |v_r| \tag{4}$$

$$x_i = \frac{n_i}{n_T} = \frac{n_i^0 + v_i \zeta}{\left(\sum_j n_j^0\right) + \Delta v \zeta} = \frac{n_i^0 + v_i \zeta}{\left(\sum_{j<i} n_j^0\right) + n_i^0 + \left(\sum_{j>i} n_j^0\right) + \Delta v \zeta} \tag{5}$$

To show how these equations can be applied, we consider the reaction given below in Eq. 6. Rows (i) and (ii) indicate the number of moles of the constituents at time 0

¹ At equilibrium Q_x is equal to the equilibrium constant K_x for an ideal gas system at constant P and T. There are other forms of Q and K that could be used to develop the present theory, for example those based on molar concentration namely Q_c and K_c or on mole numbers (Q_n, K_n). However, we have found that Q_x and K_x are the most useful for our purposes. Indeed, Q_x has proved to be the essential quantity in describing the equilibrium of an ideal gas system at constant P and T. The relationships between Q_x, K_x and Q_c, Q_n, K_c, K_n are given below: $K_P = K_x P^{\Delta v}$ and $Q_c = Q_n/V^{\Delta v} = Q_x (P/RT)^{\Delta v}$ since $PV = nRT$ and $P_i = (n_i/V)RT = [n_i/(n_T RT/P)]RT = x_i P$.

and time t , respectively. The reaction extent ζ is time related.



$$\begin{array}{cccccc} R & & 1 & & 0 & & 0 & & (i) \\ n_A = R - a\zeta & n_B = 1 - b\zeta & n_C = c\zeta & n_D = d\zeta & & & & & (ii) \end{array}$$

The values of n_T and Q_x for this reaction can be readily calculated as shown in Eqs. 7 and 8, respectively.

$$\begin{aligned} n_T &= n_A + n_B + n_C + n_D = \sum_{i=1}^N n_i \\ &= (R - a\zeta) + (1 - b\zeta) + c\zeta + d\zeta = (R + 1) + (c + d - a - b)\zeta \\ &= (n_A^\circ + n_B^\circ + n_C^\circ + n_D^\circ) + \Delta v \zeta = \left(\sum_{i=1}^N n_i^\circ \right) + \Delta v \zeta \end{aligned} \quad (7)$$

$$Q_x = \frac{x_C^c x_D^d}{x_A^a x_B^b} = \prod_{i=1}^N x_i^{v_i} = \frac{\left(\frac{c\zeta}{n_T}\right)^c \left(\frac{d\zeta}{n_T}\right)^d}{\left(\frac{R-a\zeta}{n_T}\right)^a \left(\frac{1-b\zeta}{n_T}\right)^b} = (n_T)^{-\Delta v} \prod_{i=1}^N \left(n_i^0 + v_i \zeta\right)^{v_i} \quad (8)$$

Thus, values of Q_x and n_T for any reaction can be similarly calculated with reference to the general form of Eqs. 1 and 3.

We now detail the six theorems that comprise our chemical equilibrium system. All the theorems are based on the premise that the value of the reaction quotient Q_x at equilibrium is constant, defined as the equilibrium constant, K_x , whatever the initial conditions.

Theorem 1 *The reaction quotient increases or remains unchanged (i.e. never decreases) as a reaction proceeds forward and decreases or remains unchanged (i.e. never increases) as the reaction proceeds backward. [6,7]*

Theorem 1 is important because it enables the direction of chemical shift to be established. In an equilibrium for an ideal gas system at constant P and T , Q_x can be related to the equilibrium constant K_x . When Q_x differs from K_x , then the reaction extent ζ will be changed until Q_x becomes equal to K_x . i.e. when Q_x is greater than K_x , the reaction extent will be changed to reduce Q_x until it becomes equal to K_x . When Q_x is less than K_x , ζ , will be changed to increase Q_x until it becomes equal to K_x . The facts expressed by Theorem 1 can be described mathematically by Eq. 9.

$$\left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_i} \geq 0 \quad (9)$$

Clearly, Theorem 1 means that a forward reaction always increases the product of concentrations to the coefficient power of products $\prod_p x_p^{v_p}$ and decreases that of

reactants $\prod_r x_r^{v_r}$ while a backward reaction always decreases $\prod_p x_p^{v_p}$ and increases $\prod_r x_r^{v_r}$. The validity of Theorem 1 is obvious for single phase liquid reactions. However, although it is taken for granted in most classical treatments that Theorem 1 is universally applicable, this is not obviously true. For example, a change in reaction extent ζ will affect both the numerator n_i and the denominator n_T in the expression of x_i for reactant or product (Eq. 5). Equation 9 can be developed in two ways (Appendix 1), dependent on whether the denominator D_x or the numerator N_x of Q_x (Eq. 1) is kept constant with the results shown in Eqs. 10 and 11 respectively.

$$\left(\frac{\partial Q_x}{\partial \zeta}\right)_{D_x} = \sum_{i=1}^N \frac{Q_x v_i^2}{n_i} > 0 \quad (10)$$

Indeed as shown by Eq. 10, the forward reaction will increase Q_x if we consider only the numerator N_x of Q_x in Eq. 1 because D_x is constant in Eq. 10. However, the forward reaction will also have the effect of decreasing Q_x because of the change in D_x as shown in Eq. 11.

$$\left(\frac{\partial Q_x}{\partial \zeta}\right)_{N_x} = -\frac{Q_x \Delta v^2}{n_T} < 0 \quad (11)$$

The effect shown in Eq. 11 is independent of whether Δv is positive or negative because it involves the square of Δv . These two effects, described by Eqs. 10 and 11, are opposite to each other. In order to show that Theorem 1 is correct, it is necessary to prove that the effect shown in Eq. 10 is dominant as illustrated in Eq. 12. Equation 12 is an expanded form of Eq. 9. Some background information concerning Eq. 12 is given in Appendix 1.

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

The forward reaction will increase N_x (Eq. 10) and as this effect is independent of Δv , it will also increase Q_x , while the effect of the forward reaction on D_x will decrease Q_x whatever the sign of Δv (Eq. 11). If Δv is positive, n_T will increase, as will D_x , because of the positive exponent. On the other hand, if Δv is negative, n_T will decrease by the forward reaction, but the change in D_x will still cause a decrease in Q_x because of the negative exponent. It is thus confirmed intuitively that on changing ζ , the effects on the value of Q_x of subsequent variations in N_x and D_x , are opposite. The same situation occurs when ζ is decreased. Which of these two opposite effects, shown in Eqs. 10 or 11, is greater is not easy to determine as it cannot be judged intuitively. So it is necessary to provide a mathematical proof for Eq. 12 to show that Theorem 1 is valid in all circumstances. Clearly a deductive proof would be preferable but, to our knowledge, only one based on mathematical induction is to be found in the literature [6]. We note that Eq. 12 is very similar to the Schwarz inequality [10–16]

given as Eq. 13 and so have developed the deductive proof shown below. Detailed information about the Schwarz inequality is given in Appendix 5.

$$\left(\sum_{i=1}^N a_i^2\right) \sum_{i=1}^N b_i^2 - \left(\sum_{i=1}^N a_i b_i\right)^2 \geq 0 \quad (13)$$

2.1 Proof P1 for Theorem 1

It should be noted that n_i , n_T , x_i and Q_x cannot be negative and are therefore ≥ 0 . If we define a_i and b_i as follows.

$$a_i = \sqrt{n_i}; \quad b_i = \frac{v_i}{\sqrt{n_i}} \quad (14)$$

By inserting the above definitions into Eq. 13, it can be seen that Eq. 12 is obtained, as shown by Eq. 15.

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

Since Eq. 12 can be rearranged in the form shown by Eq. 16, it is proven as indeed is Eq. 9 and therefore Theorem 1 is validated.

$$\frac{1}{\sum_{i=1}^N n_i} \left\{ \left(\sum_{i=1}^N n_i \right) \sum_{j=1}^N \frac{v_j^2}{n_j} - \left(\sum_{i=1}^N v_i \right)^2 \right\} \geq 0 \quad (16)$$

Although the Schwarz inequality is trivial in mathematics, its application here to chemical equilibrium provides significant new insights. After the connection between the Schwarz inequality and Theorem 1 is realized, all proofs for the Schwarz inequality found in the literature and repeated in Appendix 5, can be adapted to prove Theorem 1. Several different proofs for Theorem 1 are given below, because although one Proof P1, given above, is clearly sufficient to prove the theorem, in this case the alternatives, Proofs P2, P3 and P4, provide useful elucidation of different chemical concepts.

2.2 Proof P2 for Theorem 1

Theorem 1 can also be proved directly from Eq. 16 by expansion of the two terms in the curly brackets via Eqs. 17 and 18 respectively.

$$\begin{aligned} \left(\sum_{i=1}^N n_i\right) \sum_{j=1}^N \frac{v_j^2}{n_j} &= \sum_{j=1}^N \frac{\left(\sum_{i=1}^N n_i\right) v_j^2}{n_j} = \sum_{i=1}^N \sum_{j=1}^N \left(n_i \frac{v_j^2}{n_j}\right) \\ &= \sum_i \sum_{j=i} \frac{n_i v_j^2}{n_j} + \sum_i \sum_{j<i} \frac{n_i v_j^2}{n_j} + \sum_i \sum_{j>i} \frac{n_i v_j^2}{n_j} \\ &= \sum_i v_i^2 + \sum_i \sum_{j>i} \left(\frac{n_j v_i^2}{n_i} + \frac{n_i v_j^2}{n_j}\right) \end{aligned} \quad (17)$$

$$\left(\sum_{i=1}^N v_i\right)^2 = \sum_i v_i^2 + 2 \sum_i \sum_{j>i} v_i v_j \quad (18)$$

Using the results obtained in Eqs. 17 and 18 by inserting them back into Eq. 16, and noting that n_i cannot be negative, we obtain Eq. 19 and therefore Theorem 1 is proved.

$$\sum_{j=1}^N \frac{\left(\sum_{i=1}^N n_i\right) v_j^2}{n_j} - \left(\sum_{i=1}^N v_i\right)^2 = \sum_i \sum_{j>i} \frac{(n_i v_j - n_j v_i)^2}{n_i n_j} \geq 0 \quad (19)$$

When Eq. 20 is satisfied for all i and j , the equals sign in Eq. 19 pertains.

$$\frac{n_i}{n_j} = \frac{v_i}{v_j} \quad (20)$$

So when Eq. 20 is true, then Eq. 19 is reduced to Eq. 21.

$$\sum_i \sum_{j>i} \frac{(n_i v_j - n_j v_i)^2}{n_i n_j} = 0 \quad (21)$$

In this context, we note that there is an error in the proof for Eq. 12 given in ref. [6], as it concludes with >0 rather than the correct ≥ 0 in the final equation. This error is discussed further in Appendix 2. The equals sign does apply in some circumstances. For example, if only one side of the chemical equation contains gaseous species, with solid or liquid species on the other side, then Eq. 20 can be satisfied. If there is only one active species in the reaction system, the validity of Eq. 21 is obvious from the Schwarz inequality, Eq. 13. For example, when CaCO_3 is decomposed to CaO and CO_2 at constant T and P , Q_x is a constant with respect to the reaction extent. Theorem 1 can also be successfully used to analyze the equilibrium shift for the decomposition

of CaCO_3 if the pressure changes but this will not be detailed here. If gaseous species exist on both sides, then Eq. 20 can never be satisfied since v_i will have opposite signs for reactant and product. Equation 20 is easily derived from Eq. 21. However, Eq. 20 cannot readily be obtained from Proof P1, which is an indication in this case of the advantages of establishing multiple mathematical proofs.

2.3 Proof P3 for Theorem 1

Theorem 1 can also be validated by considering the simple chemical reaction described by Eq. 6. From Eqs. 6 and 12 we can generate Eq. 22.

$$\begin{aligned} \frac{1}{Q_x} \left(\frac{\partial Q_x}{\partial \zeta} \right) &= \frac{c+d}{\zeta} + \frac{a^2}{R-a\zeta} + \frac{b^2}{1-b\zeta} - \frac{\Delta v^2}{1+R+\Delta v\zeta} \\ &= \frac{(c+d)(1+R+\Delta v\zeta) - \Delta v^2\zeta}{\zeta(1+R+\Delta v\zeta)} + \frac{a^2(1-b\zeta) + b^2(R-a\zeta)}{(R-a\zeta)(1-b\zeta)} \end{aligned} \quad (22)$$

From Eq. 22 we obtain

$$\begin{aligned} \frac{1}{Q_x} \left(\frac{\partial Q_x}{\partial \zeta} \right)_R &= \frac{[1+R+(a+b)\zeta](c+d) - (a+b)^2\zeta}{\zeta(1+R+\Delta v\zeta)} \\ &+ \frac{[a^2(1-b\zeta) + b^2(R-a\zeta)][1+R+(c+d)\zeta - (a+b)\zeta]}{(1+R+\Delta v\zeta)(1-b\zeta)(R-a\zeta)} \\ &= \frac{[1+R+(a+b)\zeta](c+d)}{\zeta(1+R+\Delta v\zeta)} + \frac{[a^2(1-b\zeta) + b^2(R-a\zeta)](c+d)\zeta + k}{(1+R+\Delta v\zeta)(1-b\zeta)(R-a\zeta)} \end{aligned} \quad (23)$$

where k is given by Eq. 24.

$$\begin{aligned} k &= [1+R-(a+b)\zeta][a^2(1-b\zeta) + b^2(R-a\zeta)] - (a+b)^2(R-a\zeta)(1-b\zeta) \\ &= [(1-b\zeta) + (R-a\zeta)][a^2(1-b\zeta) + b^2(R-a\zeta)] - (a+b)^2(R-a\zeta)(1-b\zeta) \\ &= a^2(1-b\zeta)^2 + b^2(R-a\zeta)^2 - 2ab(R-a\zeta)(1-b\zeta) \\ &= [a(1-b\zeta) - b(R-a\zeta)]^2 = (a-bR)^2 \end{aligned} \quad (24)$$

By inserting the value for k obtained in Eq. 24 back into Eq. 23, Eq. 25 is obtained.

$$\begin{aligned} \frac{1}{Q_x} \left(\frac{\partial Q_x}{\partial \zeta} \right)_R &= \frac{[1+R+(a+b)\zeta](c+d)}{\zeta(1+R+\Delta v\zeta)} \\ &+ \frac{[a^2(1-b\zeta) + b^2(R-a\zeta)](c+d)\zeta + (a-bR)^2}{(1+R+\Delta v\zeta)(1-b\zeta)(R-a\zeta)} \geq 0 \end{aligned} \quad (25)$$

Since ζ ($= n_C/c$, or n_D/d), n_A ($= R - a\zeta$), n_B ($= 1 - b\zeta$), and n_T are greater than 0, it is easy to see that the ≥ 0 relationship in Eq. 25 is justified. The advantage of this Proof P3 is that it is based primarily on the initial mole ratio and so is consistent with Theorem 5 as is demonstrated in part II of this work. A different derivation of Eq. 25 expressed in a more general form is given in Appendix 3.

2.4 Proof P4 for Theorem 1

Theorem 1 can also be proved by using concepts from thermodynamics in which for example a chemical reaction can be described by Eq. 26.

$$\left(\frac{\partial G}{\partial \zeta}\right)_{T,P,n_j^0} = RT \ln Q_x + \sum_i v_i \mu_i^0(T, P) \quad (26)$$

where the Gibbs energy G is a state variable, thus it is only a function of T , P and x_j for an ideal gas system. μ_i^0 is the standard chemical potential for species i . For an equilibrium system at a constant T and P , the equilibrium value of Q_x can be denoted by K_x and as $\left(\frac{\partial G}{\partial \zeta}\right)_{T,P,n_j^0} = 0$ is satisfied when equilibrium is reached, we can simplify Eq. 26 to generate Eq. 27.

$$0 = RT \ln K_x + \sum_i v_i \mu_i^0(T, P) \quad (27)$$

which can be rearranged to give:

$$RT \ln K_x = - \sum_i v_i \mu_i^0(T, P) \quad (28)$$

Differentiating Eq. 26 with respect to ζ for the system at any T and P , we obtain Eq. 29.

$$\frac{RT}{Q_x} \left(\frac{\partial Q_x}{\partial \zeta}\right)_{T,P,n_j^0} = \left(\frac{\partial^2 G}{\partial \zeta^2}\right)_{T,P,n_j^0} \quad (29)$$

G is a minimum at equilibrium for an infinitesimal process at constant T and P . It is implied by Eq. 30, i.e. if equilibrium has not been reached, that a spontaneous reaction, either forward or back, will take place to reduce G to a minimum.

$$\left(\frac{\partial^2 G}{\partial \zeta^2}\right)_{T,P,n_j^0} \geq 0 \quad (30)$$

Inserting the thermodynamic formula of Eq. 30 into Eq. 29, we obtain Eq. 9 and thus Theorem 1 is proved from thermodynamic principles. If a condensed phase is involved, x_i does not refer to the mole fraction in the condensed phase, rather it refers

to the mole fraction of the gas that equilibrates with the condensed phase. But this does not affect the validity of this proof since we are only concerned with Eq. 9.

Theorem 1 is also important because it enables the derivation of some thermodynamic conclusions. For example, inserting Eq. 9 into Eq. 29, we obtain Eq. 30 since Q_x is positive. Thus Eq. 30, which represents the thermodynamic condition for spontaneous reaction, is proved from Eq. 9 which can be derived independently from mathematics.

The above discussions are valid for gaseous systems at constant T and P. However, even if P is changed, these conclusions concerning Q_x are still relevant. For example, K_p is always constant at constant T. If $\Delta\nu > 0$, then increasing P will decrease K_x according to $K_p = K_x P^{\Delta\nu}$, and Theorem 1 predicts that the equilibrium will shift backwards to adjust the Q_x to the new K_x . If $\Delta\nu < 0$, increasing P will increase K_x , and Theorem 1 predicts that the equilibrium will shift forwards. From the behavior of Q_x , it is possible to subsequently expand the theory in a logical fashion to produce our coherent theoretical system.

Theorem 2 *Adding a species in a gaseous equilibrium system at constant temperature and pressure will affect both the denominator D_x and the numerator N_x of Q_x (Eq. 1) and as a result it will cause two effects.*

- (2a) *On increasing D_x by adding a reactive species, while theoretically² supposing N_x remains unchanged, the equilibrium would respond by shifting to the side of the chemical equation for which the sum of coefficients is the greater.*
- (2b) *Conversely on increasing N_x by adding a reactive species, while theoretically² supposing D_x remains unchanged, the equilibrium would respond by shifting to the side of reducing the amount of that species.*

A corresponding formalism of Theorem 2 for removing a species from the equilibrium system can be readily obtained. Let us consider the effect on Q_x of changing D_x and N_x in Proofs P5 and P6, respectively.

2.5 Proof P5 for Theorem 2a

By differentiating Q_x with respect to n_i while keeping N_x and the reaction extent constant, Eq. 31 is obtained. The effect expressed in Eq. 31 is similar to that expressed in Eq. 11 as it indicates that $-\frac{\Delta\nu dn_i}{n_T}$ represents the effect on Q_x of changing D_x by adding species i while keeping N_x and the reaction extent unchanged.

$$\left(\frac{\partial Q_x}{\partial n_i}\right)_{\zeta, N_x} = -Q_x(n_i) \frac{\Delta\nu}{n_T} \quad (31)$$

It can be seen from Eq. 31 that the addition³ of species i will decrease Q_x when $\Delta\nu > 0$. Then, the forward reaction takes place according to Theorem 1 to restore

² It should be noted that both 2a and 2b are theoretical situations. In practice when a reactive species is added to a system, if D_x is increased, then N_x cannot remain unchanged and vice versa.

³ The same argument pertains for the alternative scenario when species i is removed from the equilibrium but this is omitted here for simplicity.

Q_x to K_x . Adding species i will increase Q_x when $\Delta v < 0$, and the backward reaction will take place according to Theorem 1 to restore Q_x to K_x . Thus, the result in both cases is that adding species i will shift the equilibrium toward the side of the chemical reaction with the greater sum of coefficients. Theorem 2a is thus proven.

The same result can be obtained from another point of view. Consider the effect of changing dn_i on a system which is in equilibrium. If we only consider the effect of changing D_x , the added species will dilute all the species. Hence if only this dilution is considered and the effect of an increase in numerator n_i on x_i is ignored, $\prod_j x_j^{v_j}$, the product of concentrations to their coefficient powers, will be reduced more on the side of the chemical equation with the larger sum of coefficients. Now if the reaction responds according to Theorem 1, it will proceed toward the side with the larger sum of coefficients in order to balance the changes caused by the addition. Theorem 2a, the effect of changing the denominator of Q_x on the shift in equilibrium, is thus proven as previously and it can be expressed alternatively as:

(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.*

2.6 Proof P6 for Theorem 2b

By differentiating Q_x with respect to n_i while keeping D_x and the reaction extent unchanged, Eq. 32 is obtained. The effect expressed in Eq. 32 is similar to that expressed in Eq. 10. Thus $\frac{v_i dn_i}{n_i}$ in Eq. 32 represents the effect of changing N_x by adding species i , while keeping the reaction extent and D_x constant. Adding product i will increase Q_x since $v_i > 0$, while on the other hand adding reactant i will decrease Q_x since $v_i < 0$. Theorem 2b can thus be easily proved from Eq. 32 and Theorem 1.

$$\left(\frac{\partial Q_x}{\partial n_i} \right)_{\zeta, D_x} = Q_x(n_i) \frac{v_i}{n_i} \quad (32)$$

A more intuitive proof, relevant for chemists, is provided in Appendix 4. The significance of Theorem 2 is discussed further in part II, sections 2.2.3.2 through to 2.2.3.5.

Theorem 3

(3a) *The change of an intensive variable caused by changing its corresponding extensive variable is smaller if chemical equilibrium is maintained than if no reaction can take place in the system.*

Theorem 3a can be stated alternatively as:

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

By definition, an intensive variable is a variable that is only a function of the state of the system, while an extensive variable is also a linear function of the amount of the

species in the system. Theorem 3 [8] is more rigorous than the Le Chatelier principle which is just a principle, not a theorem, since it is not universally valid. If an intensive variable and an extensive variable are interconnected, they can be expressed in a partial derivative containing the two variables. Considering the intensive variables x_i (or Q_x) and pressure P respectively with their corresponding extensive variables n_i and volume V , Theorem 3 can be expressed innovatively by Eqs. 33–35.

$$\left(\frac{\partial x_i}{\partial \zeta}\right)_{n_i} \left(\frac{\partial \zeta}{\partial n_i}\right)_{Q_x} \left(\frac{\partial n_i}{\partial x_i}\right)_{\zeta, n_j} = -1 \quad (33)$$

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

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

Here we provide a concise, uniform and elegant mathematical expression for Theorem 3. Equations 33–35 express very basic mathematical rules for three related variables as shown in Proof 7. How these simple mathematical relationships relate to the chemistry expressed in Theorem 3 are given in detail in Part II of this work [9].

2.7 Proof P7 Eqs. 33–35 stand alone as a mathematical rule

In an equilibrium system, x_i and Q_x are functions of n_i and ζ as expressed by Eqs. 36 and 37. P is a function of V , ζ , and entropy S as shown in Eq. 38.

$$x_i = x_i(n_i, \zeta) = x_i[n_i, \zeta(n_i, Q_x)] \quad (36)$$

$$Q_x = Q_x(n_i, \zeta) = Q_x[n_i, \zeta(n_i, \Delta G)] = Q_x\left[n_i^0, \zeta\left(n_i^0, K_x\right)\right] \quad (37)$$

$$P = P(S, V, \zeta) = P[S, V, \zeta(V, A)] \quad (38)$$

Differentiating Eqs. 36–38, we obtain Eqs. 39–41, respectively.

$$dx_i = \left(\frac{\partial x_i}{\partial n_i}\right)_{\zeta} dn_i + \left(\frac{\partial x_i}{\partial \zeta}\right)_{n_i} \left(\frac{\partial \zeta}{\partial n_i}\right)_{Q_x} dn_i \quad (39)$$

$$dQ_x = \left(\frac{\partial Q_x}{\partial n_i}\right)_{\zeta} dn_i + \left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_i} \left(\frac{\partial \zeta}{\partial n_i}\right)_{K_x} dn_i \quad (40)$$

$$dP = \left(\frac{\partial P}{\partial V}\right)_{S, \zeta} dV + \left(\frac{\partial P}{\partial \zeta}\right)_{S, V} \left(\frac{\partial \zeta}{\partial V}\right)_{S, A} dV \quad (41)$$

The mathematical relationships, described by Eqs. 33–35, can easily be obtained by setting the left hand sides of Eqs. 39–41 equal to zero. Thus Theorem 3 is proven. That $dQ_x = 0$ in Eq. 40 specifies the condition for equilibrium shift which refers a

transition from an old equilibrium state to a new one⁴. It is sometimes appropriate to use $\left(\frac{\partial \zeta}{\partial n_i}\right)_{K_x}$, as in Eq. 40 instead of $\left(\frac{\partial \zeta}{\partial n_i}\right)_{Q_x}$ as in Eq. 39 to denote an equilibrium system, since keeping Q_x constant is equivalent to considering an equilibrium system at K_x . $\left(\frac{\partial \zeta}{\partial n_i}\right)_{Q_x}$ is such a well-used mathematical expression that the above mentioned property of Q_x at equilibrium is easily overlooked.

Theorem 4 *When a species is added to a system, the new equilibrium concentration of that species will never decrease, independent of whether the chemical equilibrium is shifted to produce or to consume more of that species. When a species is removed from a system, the new equilibrium concentration of that species will never increase.*

When a species has been added to a system, the chemical equilibrium can shift either to produce or consume more of that species. However, the new equilibrium concentration of that species can never be reduced to a value lower than the original equilibrium value. Theorem 4 is therefore complementary to Theorem 3 in that it defines the amount by which the chemical equilibrium can be shifted.

Theorem 4 is usually taken for granted as from Eq. 27 and Fig. 1 in ref. [17], perhaps because of the intuitive belief that adding a species to an equilibrium system will definitely result in an increase in its concentration. But this is not obvious. The proof for Theorem 3 given in ref. [8] is correct only because Theorem 4 is assumed to be true. If Theorem 4 is not true, then the proof for Theorem 3 in ref. [8] cannot be valid. Theorem 4 can be formulated from Eq. 42 while keeping Q_x constant which is equivalent to keeping $Q_x = K_x$ as an equilibrium condition. This proof also involves the Schwarz inequality.

⁴ From theorem 4 and Eq. 39 we note that $\frac{dx_i}{dn_i} = \left(\frac{\partial x_i}{\partial n_i}\right)_{Q_x} \geq 0$ must be satisfied for an equilibrium shift to occur. However the maximum ability of an equilibrium shift to reduce the change in x_i by adding a species occurs when $\frac{dx_i}{dn_i} = \left(\frac{\partial x_i}{\partial n_i}\right)_{Q_x} = 0$. $\frac{dx_i}{dn_i} = \left(\frac{\partial x_i}{\partial n_i}\right)_{Q_x} < 0$ is impossible for an equilibrium shift by theorem 4. The same discussion applies to Eq. 41. Since $\left(\frac{\partial x_i}{\partial n_i}\right)_{\zeta, n_j}$ in Eq. 33 and $\left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_j}$ in Eq. 34 are always positive and $\left(\frac{\partial P}{\partial V}\right)_{S, \zeta}$ is always negative, Eq. 33–34 can be written similarly to Eqs. 1, 3, and 5 in part II of this work, e.g. as:

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

$$\left(\frac{\partial \zeta}{\partial n_i}\right)_{K_x} \left(\frac{\partial n_i}{\partial Q_x}\right)_{\zeta, n_j} < 0 \tag{II-3}$$

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

2.8 Proof P8 for Theorem 4

From Eqs. 39 and 40 for constant Q_x we can generate Eq. 42.

$$\left(\frac{\partial x_i}{\partial n_i}\right)_{Q_x} = \left(\frac{\partial x_i}{\partial n_i}\right)_{\zeta} + \left(\frac{\partial x_i}{\partial \zeta}\right)_{n_i} \left(\frac{\partial \zeta}{\partial n_i}\right)_{Q_x} = \left(\frac{\partial x_i}{\partial n_i}\right)_{\zeta} - \left(\frac{\partial x_i}{\partial \zeta}\right)_{n_i} \left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_i^0} \zeta \quad (42)$$

From Eq. 5 we can obtain Eqs. 43 and 44.

$$\left(\frac{\partial x_i}{\partial n_i^0}\right)_{\zeta} = \left(\frac{\partial \frac{n_i^0 + v_i \zeta}{(\sum_j n_j^0) + \Delta v \zeta}}{\partial n_i^0}\right)_{\zeta} = \frac{1 - x_i}{n_T} > 0 \quad (43)$$

$$\left(\frac{\partial x_i}{\partial \zeta}\right)_{n_j} = \left(\frac{\partial \frac{n_i^0 + v_i \zeta}{(\sum_j n_j^0) + \Delta v \zeta}}{\partial \zeta}\right)_{n_j} = x_i \left(\frac{v_i}{n_i} - \frac{\Delta v}{n_T}\right) \quad (44)$$

Inserting Eqs. 43, 44, 59, and 82 into 42, we obtain 45.

$$\begin{aligned} \left(\frac{\partial x_i}{\partial n_i}\right)_{Q_x} &= \frac{1 - x_i}{n_T} - \frac{v_i - \Delta v x_i}{n_T} \left(\frac{\partial Q_x}{\partial n_i^0}\right)_{\zeta} \\ &= \frac{1 - x_i}{n_T} - \frac{v_i - \Delta v x_i}{n_T} \frac{Q_x \frac{v_i - \Delta v x_i}{n_i}}{\left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_i^0}} \\ &= \frac{1 - x_i}{n_T} - \frac{(v_i - \Delta v x_i)^2}{n_T n_i \left[\sum_j \frac{v_j^2}{n_j} - \frac{\Delta v^2}{n_T}\right]} = \frac{(1 - x_i) \left[\sum_j \frac{v_j^2}{n_j} - \frac{\Delta v^2}{n_T}\right] - \frac{(v_i - \Delta v x_i)^2}{n_i}}{n_T \left[\sum_j \frac{v_j^2}{n_j} - \frac{\Delta v^2}{n_T}\right]} \\ &= \frac{\left[\sum_j \frac{v_j^2}{n_j} - \frac{\Delta v^2}{n_T}\right] - \left[x_i \sum_{j \neq i} \frac{v_j^2}{n_j} + \frac{v_i^2}{n_T}\right] + x_i \frac{\Delta v^2}{n_T} - \frac{v_i^2}{n_i} + \frac{\Delta v \cdot v_i}{n_T} + \frac{v_i^2 + v_i \sum_{j \neq i} v_j}{n_T} - x_i \frac{\Delta v^2}{n_T}}{n_T \left[\sum_j \frac{v_j^2}{n_j} - \frac{\Delta v^2}{n_T}\right]} \\ &= \frac{(1 - x_i) \sum_{j \neq i} \frac{v_j^2}{n_j} + \frac{\Delta v(v_i - \Delta v)}{n_T} + \frac{v_i \sum_{j \neq i} v_j}{n_T}}{n_T \left[\sum_j \frac{v_j^2}{n_j} - \frac{\Delta v^2}{n_T}\right]} = \frac{(1 - x_i) \sum_{j \neq i} \frac{v_j^2}{n_j} - \frac{\Delta v \sum_{j \neq i} v_j}{n_T} + \frac{v_i \sum_{j \neq i} v_j}{n_T}}{n_T \left[\sum_j \frac{v_j^2}{n_j} - \frac{\Delta v^2}{n_T}\right]} \\ &= \frac{\frac{n_T - n_i}{n_T} \sum_{j \neq i} \frac{v_j^2}{n_j} - \frac{(\sum_{j \neq i} v_j)^2}{n_T}}{n_T \left[\sum_j \frac{v_j^2}{n_j} - \frac{\Delta v^2}{n_T}\right]} = \frac{\sum_{j \neq i} n_j \sum_{j \neq i} \frac{v_j^2}{n_j} - (\sum_{j \neq i} v_j)^2}{n_T \left[\sum_j n_j \sum_j \frac{v_j^2}{n_j} - (\sum_j v_j)^2\right]} \geq 0 \quad (45) \end{aligned}$$

Thus, from Eq. 15 we obtain

$$\left(\frac{\partial x_i}{\partial n_i}\right)_{Q_x} \geq 0 \quad (46)$$

For an ideal gas equilibrium system at constant T and P, K_x is a constant. The fact that Q_x is kept constant, as shown in Eq. 46, gives the required condition for a system at equilibrium since Q_x is equal to K_x . Thus, the condition that keeps Q_x constant is just the condition for equilibrium shift since the shift represents a displacement from an old equilibrium state to a new one. The \geq specification in Eq. 46 indicates that when a small amount of i is added, the new equilibrium concentration can never be lower than the old and that when a small amount of i is removed, the new equilibrium concentration can never be higher than the old. By reference to Eq. 15, we know that the final inequality as shown in Eq. 45 is valid. Thus Theorem 4 is proven. Two additional mathematical forms of Theorem 4 for an ideal gas system are described by Eqs. 47 and 48. The derivations are simple and not given here. Equation 47 describes the effects on molarity C_i of adding species i in an ideal gaseous equilibrium system at constant temperature and pressure.

$$\left(\frac{\partial C_i}{\partial n_i}\right)_{T,P,Q_p} = \left(\frac{\partial C_i}{\partial n_i}\right)_{T,P,\zeta} + \left(\frac{\partial C_i}{\partial \zeta}\right)_{T,P,n_i} \left(\frac{\partial C_i}{\partial n_i}\right)_{T,P,Q_p} = \frac{1}{V} \left[1 - \frac{\frac{v_i^2}{n_i}}{\sum_{i=1}^N \frac{v_i^2}{n_i}} \right] \geq 0 \quad (47)$$

where Q_p represents Q expressed in partial pressure. Equation 47 signifies that the reaction can never reduce C_i to a value lower than the original equilibrium value when species i is added. For an equilibrium system of an ideal gas at constant temperature

$$\left(\frac{\partial P}{\partial V}\right)_{T,Q_p} = \left(\frac{\partial P}{\partial V}\right)_{T,\zeta} + \left(\frac{\partial P}{\partial \zeta}\right)_{T,V} \left(\frac{\partial \zeta}{\partial V}\right)_{T,Q_p} = \frac{P}{V} \left[\frac{\frac{\Delta v^2}{nT}}{\sum_{i=1}^N \frac{v_i^2}{n_i}} - 1 \right] \leq 0 \quad (48)$$

An increase in V will decrease P if the equilibrium is frozen. An equilibrium shift will increase P in order to decrease the change in this intensive variable as stated by Theorem 3. Equation 48 establishes that the equilibrium shift can never raise the pressure higher than the original equilibrium value.

Theorem 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 .*

The significance of Theorem 5 is that the final effect of the equilibrium shift is the same whether an amount of species i is added at time $t = 0$ or at any subsequent time t . i.e. the original equilibrium system together with the subsequently added amount and the final total equilibrium system can be considered as the same closed system whether

the addition is at time 0 or at time t which just represent two different expressions of the same closed system. Thus, the theorem might be considered as trivial. However, it has not previously appeared in the literature and it has useful implications as can be seen from the discussions detailed in part II, sections 2.3.1 and 2.3.2.

2.9 Proof P9 for Theorem 5

For an equilibrium system, ζ is a function of n_i and Q_x .

$$\zeta = \zeta \left[n_i \left(n_i^0, Q_x \right), Q_x \right] \quad (49)$$

If we consider Q_x and ζ as an example, then from Eqs. 37 and 49, an equilibrium property can be expressed involving n_i or n_i^0 with derivatives as shown by Eqs. 50–52 with the chain rule using Eq. 2 that $n_i = n_i^0 + \zeta v_i$ and Eq. 49.

$$\left(\frac{\partial \zeta}{\partial n_i^0} \right)_{\zeta, Q_x} = \left(\frac{\partial \zeta}{\partial n_i} \right)_{\zeta, Q_x} \left(\frac{\partial n_i}{\partial n_i^0} \right)_{\zeta, Q_x} = \left(\frac{\partial \zeta}{\partial n_i} \right)_{\zeta, Q_x} \quad (50)$$

$$\left(\frac{\partial Q_x}{\partial n_i^0} \right)_{\zeta} = \left(\frac{\partial Q_x}{\partial n_i} \right)_{\zeta} \left(\frac{\partial n_i}{\partial n_i^0} \right)_{\zeta} = \left(\frac{\partial Q_x}{\partial n_i} \right)_{\zeta} \quad (51)$$

$$\left(\frac{\partial Q_x}{\partial \zeta} \right)_{n_i^0} = \left(\frac{\partial Q_x}{\partial \zeta} \right)_{n_i} \quad (52)$$

It can be seen from this proof that any relationships obtained via Eq. 2 such as those described in Eqs. 50–52 conform to Theorem 5, i.e. independent of whether the initial n_i^0 at time 0 or the final equilibrium n_i is considered.

Theorem 6 *The optimum conditions for maximizing the mole fraction of a target product p in a chemical reaction are that the ratios of the initial number of moles for reactants and products are equivalent to the ratio of their coefficients in the balanced chemical equation, respectively, ignoring product p . There are no conditions governing the initial number of moles between reactant and product.*

Even though the optimum conditions for maximizing the mole fraction of a product and fractional conversion are different chemically, they are closely related mathematically. We can show that Theorem 6 which gives the conditions for maximizing the mole fraction of a product is expressed mathematically by Eq. 53 which is similar both to Eq. 20 and to the condition for maximizing the fractional conversion of a reactant as will be discussed in part II of this work.

$$\frac{n_j}{n_k} = \frac{v_j}{v_k} \quad j \neq p; \quad k \neq p \quad (53)$$

The coefficients v_j and v_k have opposite signs for reactant and product. So, Eq. 53 only applies between reactant and reactant or between product and product but not

between reactant and product. This is reasonable because if the optimum condition is met at $t = 0$, then according to Theorem 5 the final result will be the same as if the reaction started at time t . So, Eq. 53 represents a much more general condition and there is no condition governing the ratio between reactant and product.

2.10 Proof P10 for Eq. 53

Equation 53, which is valid for any type of reaction, is proved below by the Lagrange multiple constant method which requires a variable to be optimized and necessitates some constraints. Here only one constraint is needed, namely that $Q_x = K_x$. In this case, x_p is the required variable to be optimized with respect to the initial condition n_j^0 .

$$L(n_i^0, \zeta) = x_p + \lambda(Q_x - K_x) = \frac{n_p}{n_T} + \lambda(Q_x - K_x) \tag{54}$$

The Lagrange function (Eq. 54) for the conditional maximum x_p at constant Q_x is constructed from Eqs. 1 and 5. λ is an arbitrary constant to be determined.

$$L(n_i^0, \zeta) = \frac{n_p^0 + v_p \zeta}{(\sum_i n_i^0) + \Delta v \zeta} + \lambda \left\{ \frac{\prod_i (n_i^0 + v_i \zeta)^{v_i}}{[(\sum_i n_i^0) + \Delta v \zeta]^{\Delta v}} - K_x \right\} \tag{55}$$

where p represents a product. The proof starts from arbitrary initial concentrations. The conditional optimum conditions are specified by Eqs. 56 and 57, obtained by differentiating Eq. 55, which are equivalent but refer to the different species j and k , respectively.

$$\left(\frac{\partial L}{\partial n_j^0}\right)_\zeta = \left(\frac{\partial x_p}{\partial n_j^0}\right)_\zeta + \lambda \left(\frac{\partial Q_x}{\partial n_j^0}\right)_\zeta = -\frac{x_p}{n_T} + \lambda Q_x \frac{v_j n_T - \Delta v n_j}{n_T n_j} = 0 \tag{56}$$

$$\left(\frac{\partial L}{\partial n_k^0}\right)_\zeta = \left(\frac{\partial x_p}{\partial n_k^0}\right)_\zeta + \lambda \left(\frac{\partial Q_x}{\partial n_k^0}\right)_\zeta = -\frac{x_p}{n_T} + \lambda Q_x \frac{v_k n_T - \Delta v n_k}{n_T n_k} = 0 \tag{57}$$

where j and k represent any species other than p . Subtracting Eq. 56 from Eq. 57, we generate Eq. 58, from which Eq. 53 can be obtained.

$$\begin{aligned} \lambda Q_x \frac{v_j n_T - \Delta v n_j}{n_T n_j} - \lambda Q_x \frac{v_k n_T - \Delta v n_k}{n_T n_k} &= 0 \\ \frac{v_j n_T - \Delta v n_j}{v_k n_T - \Delta v n_k} &= \frac{n_j}{n_k} \end{aligned} \tag{58}$$

Equation 53 can be derived from Eq. 58. Thus Theorem 6 is proven. A more extensive discussion for Theorem 6 is provided in part II, section 2.3.3.

3 Conclusions

A variety of mathematical approaches are developed here to systemize chemical equilibrium theory coherently and elegantly by six theorems representing the basic core of equilibrium theory. The system relies less on thermodynamics than on straightforward mathematics. The advantages of using different mathematical approaches are shown. Theorem 1 has been formulated in an original fashion using the Schwarz inequality as shown in Eq. 15. In Theorem 2 we have extracted two fundamental effects by mathematical logic. Theorem 3 is also presented with an abstract and elegant mathematical presentation. Theorem 4 is usually taken for granted in the literature [17, 18] but rigorous mathematical proofs are provided in this paper. We show that Theorem 4 is mathematically related to Theorem 1 by the Schwarz inequality via Eqs. 15 and 45. Theorem 4 is complementary to Theorem 3 in that it specifies how far an equilibrium can shift. Theorem 5 states that the properties of an equilibrium for a closed system can be expressed for any evolving state in a variety of ways. The conditions for the maximum equilibrium concentration of a product in Theorem 6 are derived more generally from the Lagrange multiple constant method. Although all the mathematical methods adopted are straightforward, they are applied innovatively here to chemical equilibrium. In part II of this work, the interconnection between the theorems and the significance of the system formed by the theorems is discussed elegantly and more examples are given to give an intuitive perception of the abstract theorems introduced here. This work demonstrates that new research in a traditional field, generally thought to have been completed, can still offer new insights [19–21].

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Appendix 1

Different proofs for Eq. 12.

Proof PA1 Method 1 for the derivation of Eq. 12

Differentiating Eq. 1 with respect to ζ gives Eq. 59.

$$\begin{aligned} \left[\frac{\partial Q_x(n_i)}{\partial \zeta} \right]_{n_i} &= \left[\frac{\partial Q_x(n_i^0 + v_i \xi)}{\partial \zeta} \right]_{n_i^0} = \left[\frac{\partial \left(\frac{\prod_{i=1}^N n_i^{v_i}}{n_T^{\Delta v}} \right)}{\partial \zeta} \right]_{n_i^0} \\ &= \sum_{i=1}^N \left[\frac{v_i^2 n_i^{v_i} \prod_{j \neq i} (n_j)^{v_j}}{n_i (\Delta n_T)^{\Delta v}} \right] - \frac{(\Delta v)^2 (n_T)^{-\Delta v} \prod_i (n_i)^{v_i}}{n_T} \end{aligned}$$

$$= \left(\sum_{i=1}^N \frac{v_i^2}{n_i} Q_x \right) - \frac{(\Delta v)^2 Q_x}{n_T} = Q_x \left[\left(\sum_{i=1}^N \frac{v_i^2}{n_i} \right) - \frac{\Delta v^2}{n_T} \right] \tag{59}$$

Note that Eq. 59 is the sum of Eqs. 10 and 11.

Proof PA2 Method 2 for the derivation of Eq. 12

Taking logs on both sides of Eq. 1, we have

$$\begin{aligned} \ln Q_x(n_i, \zeta) &= \left(\sum_{i=1}^N v_i \ln n_i \right) - \Delta v \ln n_T \\ &= \sum_{i=1}^N v_i \ln (n_i^0 + v_i \zeta) - \Delta v \ln \left[\left(\sum_{i=1}^N n_i^0 \right) + \left(\sum_{i=1}^N v_i \right) \zeta \right] \\ &= \sum_{i=1}^N v_i \ln (n_i^0 + v_i \zeta) - \Delta v \ln \left[\left(\sum_{i=1}^N n_i^0 \right) + \Delta v \zeta \right] = \ln Q_x(n_i^0, \zeta) \end{aligned} \tag{60}$$

Differentiating Eq. 60 with respect to ζ , we obtain Eq. 61

$$\frac{1}{Q_x} \left(\frac{\partial Q_x}{\partial \zeta} \right)_{n_i} = \left(\sum_{i=1}^N \frac{v_i^2}{n_i} \right) - \frac{\Delta v^2}{n_T} \tag{61}$$

The result specified in Eq. 61 is the same as that given by Eq. 12.

Proof PA3 method 3 for the derivation of Eq. 12

By series expansion of Eqs. 1, 62 is obtained.

$$Q_x(\zeta + d\zeta) = Q_x(\zeta) \frac{\prod_i \left(1 + \frac{v_i d\zeta}{n_i} \right)^{v_i}}{\left(1 + \frac{\Delta v d\zeta}{n_T} \right)^{\Delta v}} = Q_x(\zeta) \frac{1 + \sum_{i=1}^N \frac{v_i^2 d\zeta}{n_i}}{1 + \frac{(\Delta v)^2 d\zeta}{n_T}} \tag{62}$$

On further expansion of Eqs. 62, 63 is obtained.

$$\begin{aligned} Q_x(\zeta + d\zeta) &= Q_x(\zeta) \left(1 + \sum_{i=1}^N \frac{v_i^2 d\zeta}{n_i} \right) \left[1 + \frac{(\Delta v)^2 d\zeta}{n_T} \right]^{-1} \\ &= Q_x(\zeta) \left(1 + \sum_{i=1}^N \frac{v_i^2 d\zeta}{n_i} \right) \left[1 - \frac{(\Delta v)^2 d\zeta}{n_T} \right] \\ &= Q_x(\zeta) \left[1 + \left(\sum_{i=1}^N \frac{v_i^2 d\zeta}{n_i} \right) - \frac{(\Delta v)^2 d\zeta}{n_T} \right] \end{aligned} \tag{63}$$

Equation 63 can be rearranged to give Eq. 64.

$$\left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_i} = \lim_{\Delta\zeta \rightarrow 0} \frac{Q_x(n_i + dn_i) - Q_x(n_i)}{d\zeta} = Q_x(n_i) \left[\left(\sum_{i=1}^N \frac{v_i^2}{n_i} \right) - \frac{(\Delta v)^2}{n_T} \right] \quad (64)$$

One reason for the inclusion of Proof PA3 here is that the series expansion method can also be applied to the proof of Theorem 2 as shown in Appendix 4.

From Eq. 62, it is clear that $Q_x \sum_{i=1}^N \frac{v_i^2}{n_i}$, the first term on the right hand side of Eq. 64, represents the effect of change in ζ on the numerator N_x of Q_x while keeping the denominator D_x constant, just as shown in Eq. 10; and that $-Q_x \frac{\Delta v^2}{n_T}$, the second term in the right hand side of Eq. 64, represents the effect of change in ζ on D_x while keeping N_x constant, as shown in Eq. 11. These changes in N_x and D_x will always have opposite effects on Q_x as implied by the opposite signs shown in Eq. 64 or in Eqs. 10 and 11.

Appendix 2: Correction to the error in ref [6]

There is a minor error in the proof of Theorem 1 expressed in ref. [6] in which the equal case is excluded from Eq. 9. Equation 65 is written in ref. [6] where reactants are defined as 1, 2 and products as 3, 4.

$$\frac{v_1^2}{n_1} + \frac{v_2^2}{n_2} + \frac{v_3^2}{n_3} + \frac{v_4^2}{n_4} > \frac{(|v_3| + |v_4| - |v_1| - |v_2|)^2}{n_3 + n_4 + n_1 + n_2} \quad (65)$$

It was then stated that this inequality will hold since Eq. 66 is valid.

$$\frac{v_3^2}{n_3} + \frac{v_4^2}{n_4} \geq \frac{(|v_3| + |v_4|)^2}{n_3 + n_4} \quad (66)$$

or

$$n_4^2 v_3^2 + n_3^2 v_4^2 \geq 2n_3 n_4 v_3 v_4$$

To exclude the possibility of the equals sign in Eq. 65, it was reasoned in ref. [6] that the left hand side of Eq. 65 is greater than the left hand side of Eq. 66 from Eq. 67.

$$\frac{v_1^2}{n_1} + \frac{v_2^2}{n_2} + \frac{v_3^2}{n_3} + \frac{v_4^2}{n_4} > \frac{v_3^2}{n_3} + \frac{v_4^2}{n_4} \quad (67)$$

and that the right hand side of Eq. 65 is less than the right hand side of Eq. 66 as shown in 68.

$$\frac{(|v_3| + |v_4|)^2}{n_3 + n_4} > \frac{(|v_3| + |v_4| - |v_1| - |v_2|)^2}{n_3 + n_4 + n_1 + n_2} \tag{68}$$

However for certain sets of values, this equation does not hold. For example if:

$$n_1 = n_2 = n_3 = n_4 = v_3 = v_4 = 1, \quad v_1 = v_2 = 4 \tag{69}$$

Equation 68 is incorrect. Or indeed if:

$$n_3 = n_4 = v_3 = v_4 = 0, \quad n_1 = n_2 = v_1 = v_2 = 1 \tag{70}$$

Equation 65 is also incorrect since both v_1 and v_2 or both v_3 and v_4 could be zero as is the case in the example of the decomposition of CaCO_3 considered previously when discussing Theorem 1. Under these circumstances and when Eq. 20 is satisfied, the $>$ sign in Eq. 65 is replaced with an equal sign. Thus in general, the $>$ sign should be replaced by an \geq sign.

Appendix 3: A variant of Eq. 25

In the main text, Eq. 25 is expressed in terms of moles and is developed from Eqs. 6 and 12. A more general expression of Eq. 25, detailed below, can be obtained from Eq. 19, which is a natural consequence of Theorem 5.

First, we obtain Eq. 71 from Eqs. 12 and 19.

$$\begin{aligned} \frac{n_T}{Q_x} \left(\frac{\partial Q_x}{\partial \xi} \right)_{n_j^0} &= \sum_r \sum_{r' > r} \frac{(v_r n_{r'} - v_{r'} n_r)^2}{n_r n_{r'}} + \sum_r \sum_p \frac{(v_r n_p - v_p n_r)^2}{n_r n_p} \\ &+ \sum_p \sum_{p' > p} \frac{(v_p n_{p'} - v_{p'} n_p)^2}{n_p n_{p'}} \end{aligned} \tag{71}$$

We then define Eqs. 72–75 using Eqs. 2 and 6.

$$\begin{aligned} n_r v_{r'} - n_{r'} v_r &= (n_r^0 + v_r \zeta) v_{r'} - (n_{r'}^0 + v_{r'} \zeta) v_r \\ &= n_{r'}^0 v_{r'} - n_r^0 v_r \end{aligned} \tag{72}$$

$$n_r v_p - n_p v_r = (n_r^0 + v_r \zeta) v_p - (0 + v_p \zeta) v_r = v_p n_r^0 \tag{73}$$

$$n_p v_{p'} - n_{p'} v_p = (0 + v_p \zeta) v_{p'} - (0 + v_{p'} \zeta) v_p = 0 \tag{74}$$

$$\sum_p \frac{v_p^2}{n_p} = \sum_p \frac{v_p v_p}{(0 + v_p \zeta)} = \sum_p \frac{v_p}{\zeta} \tag{75}$$

By inserting Eqs. 72 through 74 into 71, we obtain

$$\frac{n_T}{Q_x} \left(\frac{\partial Q_x}{\partial \zeta} \right)_{n_j^0} = \sum_r \sum_{r' > r} \frac{(v_r n_{r'}^0 - v_{r'} n_r^0)^2}{n_r n_{r'}} + \sum_r \sum_p \frac{(n_r^0)^2 v_p^2}{n_r n_p} \tag{76}$$

Using Eq. 75 we have

$$\begin{aligned} \sum_r \sum_p \frac{(n_r^0)^2 v_p^2}{n_r n_p} &= \left(\sum_p \frac{v_p v_p}{0 + v_p \zeta} \right) \sum_r \frac{(n_r^0)^2 - v_r^2 \zeta^2 + v_r^2 \zeta^2}{n_r} \\ &= \left(\sum_p v_p \right) \sum_r \left[\frac{(n_r^0 - v_r \zeta)}{\zeta} \frac{(n_r^0 + v_r \zeta)}{v_r} \right] + \zeta \left(\sum_p \frac{v_p}{\zeta} \right) \sum_r \frac{v_r^2 \prod_{r' \neq r} n_{r'}}{\prod_{r''} n_{r''}} \end{aligned} \quad (77)$$

By inserting Eqs. 77 into 76, we obtain Eq. 78.

$$\begin{aligned} \frac{n_T}{Q_x} \left(\frac{\partial Q_x}{\partial \zeta} \right)_{n_j^0} &= \frac{\sum_r \sum_{r' > r} (n_r^0 v_{r'} - n_{r'}^0 v_r)^2 \prod_{r'' \neq r, r'} n_{r''} + \zeta \left(\sum_p v_p \right) \sum_r (v_r^2 \prod_{r' \neq r} n_{r'})}{\prod_r n_r} \\ &\quad + \left(\sum_p v_p \right) \sum_r \frac{n_r^0 - v_r \zeta}{\zeta} \geq 0 \end{aligned} \quad (78)$$

By applying the general form of Eq. 78 to the special case of Eqs. 6, then 25 is obtained.

Appendix 4: Proof PA4 for Theorem 2

In the proof of Theorem 2, the series expansion of Q_x as shown in Proof PA3 can be used.

$$\begin{aligned} Q_x(n_i + dn_i) &= \frac{(n_i + dn_i)^{v_i} \prod_{j \neq i}^N n_j^{v_j}}{(n_T + dn_j)^{\Delta v}} = \frac{\left(1 + \frac{dn_i}{n_i}\right)^{v_i} \prod_j^N n_j^{v_j}}{\left(1 + \frac{dn_j}{n_T}\right)^{\Delta v} n_T^{\Delta v}} = Q_x(n_i) \frac{\left(1 + \frac{dn_i}{n_i}\right)^{v_i}}{\left(1 + \frac{dn_j}{n_T}\right)^{\Delta v}} \\ &= Q_x(n_i) \frac{\left(1 + \frac{v_i dn_i}{n_j}\right)}{\left(1 + \frac{\Delta v dn_i}{n_T}\right)} \end{aligned} \quad (79)$$

Just like the derivation of Eq. 64 from Eq. 62, further expansion of Eq. 79 leads to Eq. 80.

$$\begin{aligned} Q_x(n_i + dn_i) &= Q_x(n_i) \frac{\left(1 + \frac{v_i dn_i}{n_j}\right)}{\left(1 + \frac{\Delta v dn_i}{n_T}\right)} = Q_x(n_i) \left(1 + \frac{v_i dn_i}{n_i}\right) \left(1 + \frac{\Delta v dn_i}{n_T}\right)^{-1} \\ &= Q_x(n_i) \left(1 + \frac{v_i dn_i}{n_i}\right) \left(1 - \frac{\Delta v dn_i}{n_T}\right) = Q_x(n_i) \left(1 + \frac{v_i dn_i}{n_i} - \frac{\Delta v dn_i}{n_T}\right) \end{aligned} \quad (80)$$

Equation 80 can be written in derivative form as Eq. 81 which can also be obtained by conventional derivative techniques as shown in Proof PA1.

$$\begin{aligned} \left(\frac{\partial Q_x}{\partial n_i}\right)_\zeta &= \lim_{\Delta n_j \rightarrow 0} \frac{Q_x(n_i + dn_i) - Q_x(n_i)}{dn_i} \\ &= Q_x(n_i) \left(\frac{v_i}{n_i} - \frac{\Delta v}{n_T}\right) = Q_x(n_i) \frac{\Delta v}{n_i} \left(\frac{v_i}{\Delta v} - x_i\right) \end{aligned} \quad (81)$$

Multiplying through, Eq. 81 is expanded to Eq. 82.

$$\left(\frac{\partial Q_x}{\partial n_i}\right)_\zeta = Q_x(n_i) \frac{v_i}{n_i} - Q_x(n_i) \frac{\Delta v}{n_T} = Q_x(n_i) \left(\frac{v_i - \Delta v x_i}{n_i}\right) \quad (82)$$

From an inspection of Eqs. 79–82, it can be concluded that the second term on the right hand side of Eq. 82 is related to the $\frac{\Delta v dn_i}{n_T}$ term in the denominator of the last term in Eq. 79. This term represents the effect on Q_x of changing the denominator D_x of Q_x by adding species i while keeping the numerator N_x and the reaction extent unchanged and can be represented by Eq. 31.

Similarly the first term on the right hand side of Eq. 82 is related to the $\frac{v_i dn_i}{n_i}$ term in the numerator of the last term in Eq. 79. It represents the effect on Q_x of changing the numerator by adding i while keeping constant both the reaction extent and the denominator and can therefore be represented as Eq. 32 from the conventional differentiation technique.

The two effects shown by Eqs. 31 and 32 are thus revealed more explicitly by series expansion techniques as shown in Eq. 79. It shows that different mathematical methods have specific merits.

Appendix 5: Proofs of the Schwarz inequality

Since the proofs will be unfamiliar to many chemists, we provide details here. The following four proofs are, in our view, more understandable for chemists than those given in the literature. [10, 11]

Proof PA5 for the Schwarz inequality

Suppose the components of two vectors are:

$$\vec{A} = (a_1 \ a_2 \ \dots \ a_i \ \dots \ a_N) \quad (83)$$

$$\vec{B} = (b_1 \ b_2 \ \dots \ b_i \ \dots \ b_N) \quad (84)$$

then

$$\begin{aligned} \vec{A} \cdot \vec{B} &= |\vec{A}| \cdot |\vec{B}| \cos \hat{A}B \\ &= a_1 b_1 + a_2 b_2 + \dots + a_i b_i + \dots + a_N b_N \\ &= \sqrt{a_1^2 + a_2^2 + \dots + a_i^2 + \dots + a_N^2} \sqrt{b_1^2 + b_2^2 + \dots + b_i^2 + \dots + b_N^2} \cos \hat{A}B \end{aligned} \quad (85)$$

Square both sides and note that because $\cos \hat{A}B \leq 1$, the Schwarz inequality (Eq. 13) is proved.

Proof PA6 for the Schwarz inequality

Let

$$y_i = \frac{a_i}{\sqrt{\sum_j a_j^2}}; \quad z_i = \frac{b_i}{\sqrt{\sum_j b_j^2}} \quad (86)$$

Since

$$2y_i z_i \leq y_i^2 + z_i^2 \quad (87)$$

So

$$2 \sum_i y_i z_i \leq \sum_i y_i^2 + \sum_i z_i^2 \quad (88)$$

and

$$2 \sum_i \left(\frac{a_i}{\sqrt{\sum_j a_j^2}} \cdot \frac{b_i}{\sqrt{\sum_j b_j^2}} \right) \leq \sum_i \left(\frac{a_i}{\sqrt{\sum_j a_j^2}} \right)^2 + \sum_i \left(\frac{b_i}{\sqrt{\sum_j b_j^2}} \right)^2 = 2 \quad (89)$$

thus

$$\sum_i a_i b_i \leq \sqrt{\sum_j a_j^2} \sqrt{\sum_j b_j^2} \quad (90)$$

Square both sides and the Schwarz inequality (Eq. 13) is proved.

Proof PA7 for the Schwarz inequality

This proof is related to Proof P2 for Eq. 19.

$$\begin{aligned} \left(\sum_i a_i b_i \right)^2 &= \sum_i a_i^2 b_i^2 + \sum_i \sum_{j < i} a_i b_i a_j b_j + \sum_i \sum_{j > i} a_i b_i a_j b_j \\ &= \sum_i a_i^2 b_i^2 + 2 \sum_i \sum_{j > i} a_i b_i a_j b_j \end{aligned} \quad (91)$$

$$\begin{aligned} \sum_i a_i^2 \sum_j b_j^2 &= \sum_i a_i^2 b_i^2 + \sum_i \sum_{j<i} a_i^2 b_j^2 + \sum_i \sum_{j>i} a_i^2 b_j^2 \\ &= \sum_i a_i^2 b_i^2 + \sum_i \sum_{j<i} (a_j^2 b_i^2 + a_i^2 b_j^2) \end{aligned} \quad (92)$$

Subtracting Eqs. 91 from 92, we obtain Eq. 93

$$\begin{aligned} &\sum_i \sum_{j>i} (a_j^2 b_i^2 + a_i^2 b_j^2) - 2 \sum_i \sum_{j>i} a_i b_i a_j b_j \\ &= \sum_i \sum_{j>i} (a_i b_j - a_j b_i)^2 \geq 0 \end{aligned} \quad (93)$$

Proof PA8 for the Schwarz inequality

Since

$$\lambda^2 a_i^2 - 2a_i b_i \lambda + b_i^2 = (\lambda a_i - b_i)^2 \geq 0 \quad (94)$$

So

$$\lambda^2 \sum_i a_i^2 - 2\lambda \sum_i (a_i b_i) + \sum_i b_i^2 = \sum_i (\lambda a_i - b_i)^2 \geq 0 \quad (95)$$

The above inequality has the property

$$4 \left(\sum_i a_i b_i \right)^2 - 4 \sum_i a_i^2 \sum_i b_i^2 \leq 0 \quad (96)$$

which is the same as the Schwarz inequality.

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