

A mathematical approach to chemical equilibrium theory for gaseous systems—III: Q_p , Q_c , and Q_x

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Abstract The reaction quotient Q can be expressed in partial pressures as Q_p or in mole fractions as Q_x . Q_p is ostensibly more useful than Q_x because the related K_x is a constant for a chemical equilibrium in which T and P are kept constant while K_p is an equilibrium constant under more general conditions in which only T is constant. However, as demonstrated in this work, Q_x is in fact more important both theoretically and technically. The relationships between Q_x , Q_p , and Q_c are discussed. Four examples of applications are given in detail.

Keywords Reaction quotient · Equilibrium constant · Equilibrium displacement

1 Relationships between $\left(\frac{\partial Q_x}{\partial \xi}\right)_{n_i}$ and $\left(\frac{\partial Q_p}{\partial \xi}\right)_{n_i}$, and between $\left(\frac{\partial Q_x}{\partial \xi}\right)_{n_i}$ and $\left(\frac{\partial Q_c}{\partial \xi}\right)_{n_i}$

The reaction quotient Q_x with respect to mole fraction x_i with species i for a reaction is defined in previous parts [1,2] of this work and shown here as Eq. 1

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

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where

$$Q_n = \prod_{i=1}^N n_i^{v_i} \quad (2)$$

n_i is the number of moles of species i in the reacting system where there are a total of N species, n_T is the total number of moles in the system. v_i is the coefficient of species i in the balanced chemical equation, positive for product and negative for reactant; Δv is the sum of all the coefficients v_i in the equation.

In an ideal gas system, pressure P , volume V , and temperature T obey ideal gas laws represented by Eqs. 3 and 4 where R is a constant. n_T^0 is the total initial number of moles of all species in the system and ζ is the reaction extent.

$$PV = n_T RT = (n_T^0 + \Delta v \zeta) RT \quad (3)$$

$$P_i V = n_i RT \quad (4)$$

The counterparts of Q_x defined in partial pressure P_i and in molarity C_i are defined by Q_P and Q_C as shown in Eqs. 5 and 6, where their relationships with Q_x are also shown.

$$Q_P = \prod_{i=1}^N P_i^{v_i} = \prod_{i=1}^N (x_i P)^{v_i} = Q_x P^{\Delta v} \quad (5)$$

$$Q_C = \prod_{i=1}^N C_i^{v_i} = \prod_{i=1}^N \left(\frac{n_i}{V}\right)^{v_i} = \prod_{i=1}^N \left(\frac{n_i}{n_T RT/P}\right)^{v_i} = Q_x \left(\frac{P}{RT}\right)^{\Delta v} = Q_P \left(\frac{1}{RT}\right)^{\Delta v} \quad (6)$$

It is known from thermodynamics that at equilibrium with constant T , Q_P equals a constant K_P which is known as the equilibrium constant. This can be demonstrated by inserting equilibrium partial pressures into Eq. 5. By contrast Q_P can be any value with non-equilibrium partial pressures. From Eq. 5, Q_x is a constant at equilibrium only when T and P are kept unchanged in the chemical system. This constant is denoted as K_x to differentiate it from the non-equilibrium value of Q_x . Therefore, it can be concluded that K_x is not as useful as K_P [3]. But in fact we [1, 2] have shown that technically Q_x is a more useful quantity for any theoretical discussion of an ideal gas system. The example given below demonstrates that Q_x is theoretically a quantity of much more general utility. We have shown previously [1, 2] that the property represented by Eq. 7 is important for a closed system at constant T and P . In fact the expression is independent of T , P , and V .

$$\left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_i} = Q_x \left[\left(\sum_{i=1}^N \frac{v_i^2}{n_i} \right) - \frac{(\Delta v)^2}{n_T} \right] = Q_x \left[\left(\sum_{i=1}^N \frac{v_i^2}{n_i} \right) - \frac{\left(\sum_{i=1}^N v_i \right)^2}{n_T} \right] \geq 0 \quad (7)$$

Only at constant T, the following property relevant to Eq. 7 is obtained as Eq. 8 which is derived from Eq. 5.

$$\begin{aligned} \left(\frac{\partial Q_p}{\partial \zeta}\right)_{n_i} &= \left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_i} P^{\Delta v} + Q_x \left(\frac{\partial P^{\Delta v}}{\partial \zeta}\right)_{n_i} \\ &= \left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_i} P^{\Delta v} + Q_x \Delta v P^{\Delta v-1} \left(\frac{dP}{d\zeta}\right)_{n_i} \end{aligned} \tag{8}$$

Equation 10 is obtained from Eq. 9 since P is a function of n_T and V at constant T as shown in Eq. 3

$$\begin{aligned} P &= P(n_T, V) \tag{9} \\ dP &= \left(\frac{\partial P}{\partial n_T}\right)_V dn_T + \left(\frac{\partial P}{\partial V}\right)_{n_T} dV = \frac{RT}{V} dn_T - \frac{n_T RT}{V^2} dV \end{aligned} \tag{10}$$

Equation 11 is obtained for equilibrium conditions by dividing Eq. 10 by $d\zeta$

$$\frac{dP}{d\zeta} = \left(\frac{\partial P}{\partial n_T}\right)_V \left(\frac{\partial n_T}{\partial \zeta}\right)_{n_T^0} + \left(\frac{\partial P}{\partial V}\right)_{n_T} \left(\frac{\partial V}{\partial \zeta}\right)_{n_T} \tag{11}$$

Equation 3 can be represented generally by Eq. 12 at constant T. Equation 11 can also be obtained directly from Eq. 12.

$$P = P[n_T(n_T^0, \zeta), V(n_T, \zeta)] \tag{12}$$

Then Eq. 13 can be derived from Eq. 11 by using Eq. 3.

$$\frac{dP}{d\zeta} = \frac{RT}{V} \Delta v - \frac{n_T RT}{V^2} \frac{\Delta v RT}{P} = \frac{RT}{V} \Delta v - \frac{n_T RT}{PV} \frac{\Delta v RT}{V} = 0 \tag{13}$$

Equation 13 can then be used to simplify Eq. 8 so as to obtain Eq. 14.

$$\left(\frac{\partial Q_p}{\partial \zeta}\right)_{n_i} = \left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_i} P^{\Delta v} \tag{14}$$

Equation 14 shows that $\left(\frac{\partial Q_p}{\partial \zeta}\right)_{n_i}$ and $\left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_i}$ are closely related especially when P is also kept constant and both ζ and V are allowed to change. Thus, Eq. 7 remains the most essential expression even if only T is kept constant which shows the important role played by Q_x .

When T and V are kept constant, we can derive Eq. 15 from Eq. 10.

$$\frac{dP}{d\zeta} = \frac{RT}{V} \Delta v + 0 = \frac{n_T RT}{n_T V} \Delta v = \frac{P}{n_T} \Delta v \tag{15}$$

By inserting Eqs. 7 and 15 into Eq. 8 we derive Eq. 16 assuming that T and V are constant

$$\begin{aligned} \left(\frac{\partial Q_P}{\partial \zeta}\right)_{n_i} &= Q_x \left[\left(\sum_{i=1}^N \frac{v_i^2}{n_i} \right) - \frac{(\Delta v)^2}{n_T} \right] P^{\Delta v} + Q_x (\Delta v P^{\Delta v-1}) \left(\frac{\Delta v}{n_T} P \right) \\ &= Q_P \left[\left(\sum_{i=1}^N \frac{v_i^2}{n_i} \right) - \frac{(\Delta v)^2}{n_T} \right] + Q_P \frac{(\Delta v)^2}{n_T} = Q_P \sum_{i=1}^N \frac{v_i^2}{n_i} > 0 \end{aligned} \quad (16)$$

It is easy to see from Eq. 6 that Q_C is also a constant at equilibrium with constant T and is known as K_C . However, Q_C is usually used when both T and V are constant. Under these conditions, Eq. 17 can be obtained from Eq. 6 or derived similarly to Eq. 16.

$$\left(\frac{\partial Q_C}{\partial \zeta}\right)_{n_i} = Q_C \sum_{i=1}^N \frac{v_i^2}{n_i} > 0 \quad (17)$$

Equations 7, 16, and 17 signify that the value of Q is increased by a forward reaction and decreased by a backward reaction. As shown in part I of this work [1], Q_x is also the key in assessing the direction of the shift in chemical equilibrium even though K_x is not a constant while P is variable. If $\Delta v > 0$, then increasing P will increase Q_P according to $Q_P = Q_x P^{\Delta v}$ when the reaction in the system is frozen. Then the reaction will go backwards according to Eq. 7 to decrease Q_x in order to restore Q_P to its original value of K_P . If $\Delta v < 0$, increasing P will decrease Q_P if Q_x is kept as a constant, and the reaction will go forward in the equilibrium shift to increase Q_x in order to restore the original value of Q_P . In both situations, increasing P will result in an equilibrium shift towards the side of chemical reaction containing the smaller sum of coefficients. Similarly, from Eq. 6, $Q_c = Q_x (n_T/V)^{\Delta v}$. When V is increased and the reaction is frozen, Q_c will decrease if $\Delta_v > 0$ and increase if $\Delta_v < 0$ for constant T. This is because Q_x is a constant for a closed system when ζ is fixed. When the reaction is unfrozen, according to Theorem 7 in part I of this work [1] or Eq. 7, the equilibrium will shift toward the side with the larger sum of coefficients for the balanced chemical reaction equation. This result is exactly the same as that described by Theorem 2a introduced in part I of this work [1,2].

2 Application 1

In part I of this work [1] we derived Eq. 19 from Eqs. 7 and 18 for the Gibbs energy G of a reaction.

$$\left(\frac{\partial G}{\partial \zeta}\right)_{T,P,n_i} = \left[\sum_i v_i \mu_i^0(T, P) \right] + RT \ln Q_x \quad (18)$$

$$\left(\frac{\partial^2 G}{\partial \zeta^2}\right)_{T,P,n_i} \geq 0 \quad (19)$$

where $\mu_i^0(T, P)$ is the standard chemical potential for species i . In Eq. 17 of ref. [4] a similar equation as Eq. 19 is given but without the equal sign, i. e. with $>$ rather than \geq . This is clearly an oversimplification as it can be seen from Eqs. 16 and 17 that the equals sign can be rigorously excluded only at constant T and V as shown by Eq. 20.

$$\left(\frac{\partial^2 G}{\partial \zeta^2}\right)_{T,V,n_i} > 0 \tag{20}$$

Equations 19 and 20 signify that the Gibbs energy is a minimum at equilibrium.

3 Application 2

The molarity C_i is totally determined by n_i and ζ at constant V and thus it can be described with the function shown by Eq. 21 for reactions at constant T and V .

$$C_i = C_i(n_i, \zeta) \tag{21}$$

When species i is added into a chemical equilibrium system, the change of the molarity of species i is shown by Eq. 22.

$$dC_i = \left(\frac{\partial C_i}{\partial n_i}\right)_{\zeta} dn_i + \left(\frac{\partial C_i}{\partial \zeta}\right)_{V,n_i} d\zeta \tag{22}$$

The first term on the right of Eq. 22 describes the change in molarity caused by the addition of species for the open system if the chemical reaction involved in the system is frozen. The second term describes the change in molarity caused by the change in ζ for the closed system. The change in ζ is caused by the equilibrium shift initiated by the addition of species i . ζ is determined by n_i and Q_C , thus it can be described by Eq. 23. The amount of change in ζ indicated in Eq. 24 is determined from Eq. 23 at equilibrium with $Q_C = K_C$.

$$\zeta = \zeta(n_i, Q_C) \tag{23}$$

$$d\zeta = \left(\frac{\partial \zeta}{\partial n_i}\right)_{Q_C=K_C} dn_i \tag{24}$$

By inserting Eq. 24 into Eq. 22 we obtain Eq. 25 for equilibrium at constant T and V .

$$\left(\frac{\partial C_i}{\partial n_i}\right)_{T,V,Q_C=K_C} = \left(\frac{\partial C_i}{\partial n_i}\right)_{\zeta} + \left(\frac{\partial C_i}{\partial \zeta}\right)_{V,n_i} \left(\frac{\partial \zeta}{\partial n_i}\right)_{T,V,Q_C=K_C} \tag{25}$$

In fact Eqs. 21 and 23 can be combined into Eq. 26, while Eq. 25 can be obtained directly from Eq. 26. It is also indicated by Eq. 26 that n_i is a function of ζ and n_i^0 the initial mole number of species i .

$$C_i = C_i[n_i, \zeta(n_i, Q_C)] = C_i[n_i(n_i^0, \zeta), \zeta(n_i, Q_C)] \tag{26}$$

The terms $\left(\frac{\partial C_i}{\partial n_i}\right)_\zeta$ and $\left(\frac{\partial C_i}{\partial \zeta}\right)_{V,n_i}$ in Eq. 25 can be easily obtained as shown by Eqs. 27 and 28. Equation 27 shows that the molarity of i is increased when species i is added to an equilibrium system if the chemical reaction in the system is frozen.

$$\left(\frac{\partial C_i}{\partial n_i}\right)_\zeta = \left(\frac{\partial \frac{n_i}{V}}{\partial n_i}\right)_\zeta = \frac{1}{V} > 0 \quad (27)$$

$$\left(\frac{\partial C_i}{\partial \zeta}\right)_{V,n_i} = \left(\frac{\partial \frac{n_i^0 + v_i \zeta}{V}}{\partial \zeta}\right)_{V,n_i} = \frac{v_i}{V} \quad (28)$$

Only V , n_i and ζ will affect the value of Q_C when i is added. Thus, the term $\left(\frac{\partial \zeta}{\partial n_i}\right)_{T,V,Q_C=K_C}$ in Eq. 25 can be obtained from Eq. 29.

$$Q_C = Q_C(V, n_i, \zeta) \quad (29)$$

At constant T , Q_C is a constant under equilibrium conditions. We only consider Q_C when T and V are constant. Thus at equilibrium we can obtain Eqs. 30 and 31 from Eq. 29. Equations 6 and 17 are used in obtaining Eq. 31.

$$dQ_C = \left(\frac{\partial Q_C}{\partial n_i}\right)_{V,\zeta} dn_i + \left(\frac{\partial Q_C}{\partial \zeta}\right)_{V,n_i} d\zeta = 0 \quad (30)$$

$$\left(\frac{\partial \zeta}{\partial n_i}\right)_{T,V,Q_C=K_C} = -\frac{\left(\frac{\partial Q_C}{\partial n_i}\right)_{V,\zeta}}{\left(\frac{\partial Q_C}{\partial \zeta}\right)_{V,n_i}} = -\frac{Q_C \frac{v_i}{n_i}}{Q_C \sum_{j=1}^N \frac{v_j^2}{n_j}} \quad (31)$$

Combining Eqs. 28 and 31, we obtain Eq. 32 for the second term on the right of Eq. 25.

$$\left(\frac{\partial C_i}{\partial \zeta}\right)_{V,n_i} \left(\frac{\partial \zeta}{\partial n_i}\right)_{T,V,Q_C=K_C} = -\frac{v_i}{V} \frac{Q_C \frac{v_i}{n_i}}{Q_C \sum_{j=1}^N \frac{v_j^2}{n_j}} = -\frac{\frac{v_i^2}{n_i}}{V \sum_{j=1}^N \frac{v_j^2}{n_j}} \leq 0 \quad (32)$$

Equation 32 pertains to a closed system and its negative value indicates that the reaction proceeds to reduce the increase caused by the first term on the right of Eq. 25. When Eqs. 27 and 32 are inserted into Eq. 25, we obtain Eq. 33.

$$\left(\frac{\partial C_i}{\partial n_i}\right)_{T,V,Q_C=K_C} = \frac{1}{V} \left[1 - \frac{\frac{v_i^2}{n_i}}{\sum_{j=1}^N \frac{v_j^2}{n_j}} \right] \geq 0 \quad (33)$$

Equation 33 signifies that when species i is added at constant T and V , the new equilibrium molarity of species i will never be less than its original equilibrium molarity.

4 Application 3

For a closed system, we have

$$P = P[T, V, \zeta (T, V, Q_P)] \tag{34}$$

Equation 35 can be obtained from Eq. 34 for constant T

$$\left(\frac{\partial P}{\partial V}\right)_{T, Q_P=K_P} = \left(\frac{\partial P}{\partial V}\right)_{T, \zeta} + \left(\frac{\partial P}{\partial \zeta}\right)_{T, V} \left(\frac{\partial \zeta}{\partial V}\right)_{T, Q_P=K_P} \tag{35}$$

The first term on the right side of Eq. 35 indicates that the pressure of the system is decreased when the volume is increased as indicated by Eq. 36 where the reaction in the system is frozen.

$$\left(\frac{\partial P}{\partial V}\right)_{T, \zeta} = \left(\frac{\partial \frac{n_T RT}{V}}{\partial V}\right)_{T, \zeta} = -\frac{n_T RT}{V^2} = -\frac{P}{V} < 0 \tag{36}$$

The second term on the right side of Eq. 35 is positive as indicated by Eqs. 37 and 38 which means that the reaction in the system will proceed to increase the pressure of the system for an equilibrium shift.

$$\left(\frac{\partial P}{\partial \zeta}\right)_{T, V} = \left[\frac{\partial \left(\frac{n_T^0 + \Delta v \zeta}{V}\right) RT}{\partial V} \right]_{T, \zeta} = \frac{\Delta v RT}{V} = \frac{\Delta v n_T RT}{n_T V} = \frac{\Delta v P}{n_T} \tag{37}$$

$$\begin{aligned} \left(\frac{\partial \zeta}{\partial V}\right)_{T, Q_P=K_P} &= -\frac{\left(\frac{\partial Q_P}{\partial V}\right)_{T, \zeta}}{\left(\frac{\partial Q_P}{\partial \zeta}\right)_{T, V}} = -\frac{\left\{ \frac{\partial [Q_n \left(\frac{RT}{V}\right)^{\Delta v} 1]}{\partial V} \right\}_{T, \zeta}}{\left\{ \frac{\partial [\prod_{i=1}^N (n_i^0 + v_i \zeta)^{v_i} 1 \left(\frac{RT}{V}\right)^{\Delta v}]}{\partial \zeta} \right\}_{T, V}} \\ &= -\frac{-\frac{\Delta v Q_P}{V}}{Q_P \sum_{j=1}^N \frac{v_j^2}{n_j}} \end{aligned} \tag{38}$$

Equation 16 can be used in the derivation of Eq. 38. We obtain Eq. 39 when Eqs. 36–38 are inserted into Eq. 35. The inclusion of the \leq sign can be justified from Eq. 7.

$$\left(\frac{\partial P}{\partial V}\right)_{T, Q_P=K_P} = \frac{P}{V} \left[\frac{\left(\sum_{j=1}^N v_j\right)^2}{n_T} - 1 \right] \leq 0 \tag{39}$$

The final results from Eqs. 25 and 35 show a common feature of equilibrium, i.e. that the change of an intensive variable Y_i (C_i or P in the above example) resulting from the

change of an extensive variable $y_i(n_i$ or V) for a system at equilibrium (the term on the right side of Eqs. 25, 35, 41 or 42) is less than that for a system not at equilibrium (the first term on the left side of Eqs. 25, 35, 41 or 42). Equation 41 applies to the intensive variable x_i and its corresponding extensive variable n_i , as indicated by Eq. 40 which is derived in part I of the work [1] for equilibrium at constant T and P .

$$\begin{aligned} \left(\frac{\partial x_i}{\partial n_i}\right)_{T,P,Q_x=K_x} &= \left(\frac{\partial x_i}{\partial n_i}\right)_\zeta + \left(\frac{\partial x_i}{\partial \zeta}\right)_{n_i} \left(\frac{\partial \zeta}{\partial n_i}\right)_{T,P,Q_x=K_x} \\ &= \frac{1-x_i}{nT} - \frac{Q_x(v_i - \Delta v x_i)^2}{n_T n_i \left(\frac{\partial Q_x}{\partial \zeta}\right)_{n_i^0}} \\ &= \frac{\left(\sum_{j \neq i} n_j\right) \left[\sum_{j \neq i} \frac{v_j^2}{n_j} - \frac{\left(\sum_{j \neq i} v_j\right)^2}{\sum_{j \neq i} n_j} \right]}{n_T^2 \left[\sum_j \frac{v_j^2}{n_j} - \frac{\Delta v^2}{nT} \right]} \geq 0 \end{aligned} \quad (40)$$

$$\left| \left(\frac{\partial Y_i}{\partial y_i}\right)_{T,Q_p=K_p} \right| \leq \left| \left(\frac{\partial Y_i}{\partial y_i}\right)_{T,\zeta} \right| \quad (41)$$

From Eq. 41, Eq. 42 can be derived.

$$\left| \left(\frac{\partial y_i}{\partial Y_i}\right)_{T,Q_p=K_p} \right| \geq \left| \left(\frac{\partial y_i}{\partial Y_i}\right)_{T,\zeta} \right| \quad (42)$$

The chemistry signified by Eq. 42 can be formulated as “The change of an extensive variable caused by changing the corresponding intensive variable is larger if chemical equilibrium is maintained than if no reaction could take place in the system” [4]. The results from Eqs. 41 and 42 are just what referred by Theorem 3 [1,2].

5 Application 4

Theorem 7 For an ideal gas equilibrium system at constant T and P , the final mole fractions are only a function of K_x and the initial mole ratio, independent of whether the system is scaled up or down.

An example showing the validity of Theorem 7 was given in Table 1 from part II of the work [2]. It is demonstrated below by another example, which involves Q_x . In

Table 1 Values of reaction extent obtained from various initial moles R

R	0.2000	0.5000	1.0000	2.0000	3.0000	4.0000	5.0000
ζ	0.0766	0.1915	0.3831	0.7661	1.1492	1.5322	1.9153

this example K_x is set at 2.97 [5].

$$\begin{array}{rcll}
 2A & = & 2B + C & \\
 R & 0 & 0 & \textit{initial} \\
 R - 2\zeta & 2\zeta & \zeta & \textit{final}
 \end{array} \tag{43}$$

From Eq. 43 we obtain Eq. 44.

$$\frac{\left(\frac{2\zeta}{R+\zeta}\right)^2 \left(\frac{\zeta}{R+\zeta}\right)}{\left(\frac{R-2\zeta}{R+\zeta}\right)^2} = \frac{4\zeta^3}{(R-2\zeta)^2(R+\zeta)} = 2.97 \tag{44}$$

When the initial mole R takes various values, Table 1 shows the corresponding values of the reaction extent ζ .

When R is scaled up or down m times, it is easy to see from Eq. 44 that the reaction extent ζ must be similarly scaled. Thus, the final mole fraction distribution for all the species will be the same as shown from Eqs. 45 to 47 whatever the value of R .

$$\frac{\zeta}{R+\zeta} = \frac{\zeta_1}{R_1+\zeta_1} = \frac{\zeta_2}{R_2+\zeta_2} = \dots \tag{45}$$

$$\frac{2\zeta}{R+\zeta} = \frac{2\zeta_1}{R_1+\zeta_1} = \frac{2\zeta_2}{R_2+\zeta_2} = \dots \tag{46}$$

$$\frac{R-2\zeta}{R+\zeta} = \frac{R_1-2\zeta_1}{R_1+\zeta_1} = \frac{R_2-2\zeta_2}{R_2+\zeta_2} = \dots \tag{47}$$

As a result of this scaling, only one solution for a particular R is needed since the others can be easily obtained from Eq. 48.

$$\frac{\zeta}{R} = \frac{\zeta_1}{R_1} = \frac{\zeta_2}{R_2} = \dots \tag{48}$$

6 Conclusions

Superficially, it might be argued that conclusions based on Q_x are not reliable since K_x is only a constant if the pressure is fixed. However, Q_x is in fact more important theoretically as it has been shown in this work that it is particularly useful in developing an equilibrium theory for ideal gas systems and indeed most equilibrium problems can be solved from its consideration [6–13]. The relationships between Q_p and Q_x , and between Q_c and Q_x are discussed. Four examples where Q_x provides an essential contribution are given in detail. Of particular interest is that our rigorous proof shows that Eq. 19 should contain \geq rather than the $>$ reported in the derivation given in ref. [4]. Although the contents concerned here are elementary, it deserves the effort paid in getting more in-depth and systematic views [14]. We agree that good work, whether it is elementary or in frontier, is also educational significant [15].

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