The graphical representation of equilibrium for the isothermal and isobaric reactions of ideal gases

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The equilibrium for the isothermal and isobaric reactions of ideal gases is investigated in virtue of the intuitionistic figure. The curve $\ln Q_x \left(= \sum_i v_i \ln x_i\right) - \xi$ is similar to the curve of tangential function which has one inflection and two vertical asymptotes. The equation $\Delta G^\circ = -RT \ln Q_x$ only has one root ξ_e and it is suitable to find ξ_e by dichotomy. For non-inert substance, when $v_i / \sum_i v_i < 0$ or $v_i / \sum_i v_i > x_i^0$, to increase substance i will make an equilibrium shift in the direction to deplete substance i; when $x_i^0 > v_i / \sum_i v_i > 0$, to increase substance i will make an equilibrium shift in the direction to produce more substance i.

KEY WORDS: ideal gases, isobaric reactions, equilibrium shift, graphical representation

1. Introduction

Owing to the complexity of mathematics and the restriction of length, the discussions about the equilibrium for the isothermal and isobaric reactions of ideal gases in textbook of physical chemistry are comparatively simple and easy. For example, the shape of $\ln Q_x - \xi$ curve, the root of the equation $\Delta G^* = -RT \ln Q_{x,e}$ and the influence of non-inert substance on equilibrium, and so on, are all not involved. These problems will be discussed exhaustively and thoroughly in this paper [1–5].

2. The shape of the curve $\ln Q_x - \xi$ and the root of the equation $\Delta G^* = -RT \ln Q_{x,e}$

The equilibrium condition of the isothermal and isobaric reactions of ideal gases is

$$-\Delta G^* \big/ (RT) = \ln Q_{x,e} = \ln K_x, \tag{1}$$

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where

$$\Delta G^* = \sum_i v_i \mu_i^*, \quad \mu_i^* = \mu_i^\circ (T) + RT \ln \left(p \big/ p^\circ \right), \quad Q_x = \prod_i x_i^{v_i}. \qquad (2)$$

T is the absolute temperature, $Q_{x,e}$ the value of Q_x at equilibrium, K_x the equilibrium constant, v_i the metric coefficient of reaction substance, μ_i^* the chemical potential of pure ideal gases i, $\mu_i^\circ (T)$ the chemical potential of ideal gases i at standard state, p the pressure of reaction, p° the standard pressure, x_i the mole fraction of substance i,

$$x_i = \left(n_i^0 + v_i \xi \right) \bigg/ \left(n^0 + \xi \sum_i v_i \right), \qquad (3)$$

where $n^0 = \sum_i n_i^0$, n_i^0 is the initial mole number of substance i, ξ is the extent of reaction. So when n_i^0 is definite, by the third formula in equations (2) and (3), we know that Q_x is only the function of ξ. To find the equilibrium point of reaction is just to find the root of equation (1). Now we discuss the root of equation (1) by figure.

2.1. The asymptote of the curve ln $Q_x - \xi$

First we prove that the curve $\ln Q_x - \xi$ has two upright asymptotes. Let r denotes reactant and p denotes resultant. By $n_r = n_r^0 + v_r \xi$ we know that when $n_r = 0$,

$$\xi = -n_r^0 / v_r = n_r^0 / |v_r| = \xi_{\infty,+}, \qquad (4)$$

where $\xi_{\infty,+}$ is just the extent of reaction when the reactant reacts to the end rightward. If there are more reactants than one, then $\xi_{\infty,+}$ should adopt minimal $n_r^0 / |v_r|$, because the substance with least $n_r^0 / |v_r|$ is exhausted first. So

$$\xi_{\infty,+} = \left(n_r^0 / |v_r| \right)_{\min}. \qquad (5)$$

Analogously when the resultant reacts to the end leftward,

$$\xi_{\infty-} = - \left(n_p^0 / |v_p| \right)_{\min}. \qquad (6)$$

Supposing that v_r, n_r^0, n_r and x_r corresponding with $\xi_{\infty,+}$ is $v_r^{\#}$, $n_r^{0\#}$, $n_r^{\#}$ and $x_r^{\#}$, respectively, v_p, n_p^0, n_p and x_p corresponding with $\xi_{\infty-}$ is $v_p^{\#}$, $n_p^{0\#}$, $n_p^{\#}$ and $x_p^{\#}$, respectively. Thus when the reactant reacts to the end rightward, $x_r^{\#} \to 0$, by the third formula in equation (2), we know that

$$\ln Q_x = \sum_i v_i \ln x_i = \sum_r v_r \ln x_r + \sum_p v_p \ln x_p \approx \sum_r v_r \ln x_r \approx v_r^{\#} \ln x_r^{\#} \to +\infty.$$

$$(7)$$

Analogously when the resultant reacts to the end leftward, $x_p^{\#} \to 0$,

$$\ln Q_x \approx v_p^{\#} \ln x_p^{\#} \to -\infty. \tag{8}$$

So equations (5) and (6) are two asymptote of the curve $\ln Q_x - \xi$.

2.2. The monotonicity of the curve $\ln Q_x - \xi$

Second, we prove that $\ln Q_x$ monotonously increases with ξ. Differentiating equation (7), we obtain

$$\frac{\partial \ln Q_x}{\partial \xi} = \sum_i v_i \frac{\partial \ln x_i}{\partial \xi}. \tag{9}$$

By equation (3) we obtain

$$\ln x_i = \ln (n_i^0 + v_i \xi) - \ln \left(n^0 + \xi \sum_i v_i \right). \tag{10}$$

Differentiating equation (10), we obtain

$$\frac{\partial \ln x_i}{\partial \xi} = \frac{1}{n} \left(\frac{v_i}{x_i} - \sum_i v_i \right). \tag{11}$$

Substituting equation (11) into equation (9), we obtain

$$\frac{\partial \ln Q_x}{\partial \xi} = \frac{1}{n} \left[\sum_i \frac{v_i^2}{x_i} - \left(\sum_i v_i \right)^2 \right] = \frac{1}{n} \sum_i \left[\frac{1}{x_i} \left(v_i - x_i \sum_i v_i \right)^2 \right] > 0. \tag{12}$$

If $\sum_i v_i = 0$, inequality equation (12) is tenable. If $\sum_i v_i \neq 0$, equation (12) can be rewritten as

$$\frac{\partial \ln Q_x}{\partial \xi} = \frac{1}{n} \left(\sum_i v_i \right)^2 \sum_i \frac{1}{x_i} \left(x_i - \frac{v_i}{\sum_i v_i} \right)^2 > 0. \tag{13}$$

We can not exclude the possibility that a certain term or some terms $x_i - v_i \big/ \sum_i v_i$ in equation (13) are possibly equal to 0, but for definite reaction, some $v_i \big/ \sum_i v_i$ are positive without fail and other $v_i \big/ \sum_i v_i$ are negative without fail, and x_i are positive unvaryingly, so it is impossible that all $x_i - v_i \big/ \sum_i v_i$ in equation (13) are equal to 0. Thus the right-hand side of equation (13) are positive unvaryingly. So $\ln Q_x$ monotonously increases with ξ.

We are also able to prove that the right-hand side of equation (12) is greater than 0 by following method. Define

$$f(x_1, x_2, \ldots, x_k) = \sum_{i=1}^{k} \frac{v_i^2}{x_i} - \left(\sum_{i=1}^{k} v_i\right)^2. \tag{14}$$

Now we prove that f has the only and positive minimum. Differentiating equation (14), we obtain

$$\begin{aligned}
\mathrm{d}f &= -\sum_{i=1}^{k} \frac{v_i^2}{x_i^2} \mathrm{d}x_i = -\sum_{i=1}^{k-1} \frac{v_i^2}{x_i^2} \mathrm{d}x_i - \frac{v_k^2}{x_k^2} \mathrm{d}x_k \\
&= -\sum_{i=1}^{k-1} \frac{v_i^2}{x_i^2} \mathrm{d}x_i + \frac{v_k^2}{x_k^2} \sum_{i=1}^{k-1} \mathrm{d}x_i = -\sum_{i=1}^{k-1} \left(\frac{v_i^2}{x_i^2} - \frac{v_k^2}{x_k^2}\right) \mathrm{d}x_i. \tag{15}
\end{aligned}$$

Let $\mathrm{d}f = 0$, we obtain

$$x_i = x_k |v_i| / |v_k|. \tag{16}$$

Substituting equation (16) into $\sum_{i=1}^{k} x_i = 1$, we obtain $x_k / |v_k| = 1 / \sum_{i=1}^{k} |v_i|$; substituting this formula into equation (16), we obtain

$$x_i = |v_i| / \sum_{i=1}^{k} |v_i|. \tag{17}$$

Equation (17) is just the extremum point of f. Differentiating equation (14) twice, we obtain

$$\mathrm{d}^2 f = 2 \sum_{i=1}^{k} \frac{v_i^2}{x_i^3} (\mathrm{d}x_i)^2 > 0 \tag{18}$$

So equation (17) is the minimum point of f. Substituting equation (17) into equation (14), we obtain

$$\begin{aligned}
f_{\min} &= \left(\sum_{i=1}^{k} |v_i|\right)^2 - \left(\sum_{i=1}^{k} v_i\right)^2 = \left(\sum_p v_p + \sum_r |v_r|\right)^2 - \left(\sum_p v_p - \sum_r |v_r|\right)^2 \\
&= (a+b)^2 - (a-b)^2 > 0. \tag{19}
\end{aligned}$$

So equation (17) is the positive minimum point of f. Thus we have proved inequality equation (12) once again.

When $x_r^\# \to 0$ or $x_p^\# \to 0$, $\partial \ln Q_x / \partial \xi$ is limitless, this can be proved as follows: equation (12) can be rewritten as:

$$\frac{\partial \ln Q_x}{\partial \xi} = \frac{1}{n} \sum_i \left(\frac{v_i}{\sqrt{x_i}} - \sqrt{x_i} \sum_i v_i \right)^2 \tag{20}$$

by equation (20), we know that when $x_r^\# \to 0$,

$$\frac{\partial \ln Q_x}{\partial \xi} \approx \frac{1}{n} \left(\frac{v_r^\#}{\sqrt{x_r^\#}} \right)^2 \to +\infty, \tag{21}$$

when $x_p^\# \to 0$,

$$\frac{\partial \ln Q_x}{\partial \xi} \approx \frac{1}{n} \left(\frac{v_p^\#}{\sqrt{x_p^\#}} \right)^2 \to +\infty. \tag{22}$$

2.3. The inflexion of the curve $\ln Q_x - \xi$

Finally we prove that the curve $\ln Q_x - \xi$ has the only inflexion. Equation (12) can be rewritten as:

$$\frac{\partial \ln Q_x}{\partial \xi} = \sum_i \frac{v_i^2}{n_i} - \frac{1}{n} \left(\sum_i v_i \right)^2. \tag{23}$$

Differentiating equation (23) we obtain

$$\frac{\partial^2 \ln Q_x}{\partial \xi^2} = \frac{1}{n^2} \left(\sum_i v_i \right)^3 - \sum_i \frac{v_i^3}{n_i^2}. \tag{24}$$

Let $(\partial^2 \ln Q_x / \partial \xi^2) = 0$, we obtain

$$\frac{1}{n^2} \left(\sum_i v_i \right)^3 - \sum_i \frac{v_i^3}{n_i^2} = 0. \tag{25}$$

Equation (25) only has one solution, this can be proved as follows: when the reactant reacts to the end rightward, $n_r^\# \to 0$, so by equation (24), we know that

$$\frac{\partial^2 \ln Q_x}{\partial \xi^2} \approx -\frac{v_r^{\#3}}{n_r^{\#2}} \to +\infty. \tag{26}$$

Analogously when the resultant reacts to the end leftward, $n_p^{\#} \to 0$,

$$\frac{\partial^2 \ln Q_x}{\partial \xi^2} \approx -\frac{v_p^{\#3}}{n_p^{\#2}} \to -\infty. \tag{27}$$

Again $\partial^2 \ln Q_x/\partial \xi^2$ monotonously increases with ξ (see latter demonstration), so equation (25) only has one solution, viz. the curve $\ln Q_x - \xi$ only has one inflexion.

Now we prove that $\partial^2 \ln Q_x/\partial \xi^2$ monotonously increases with ξ. Differentiating equation (24), we obtain

$$\frac{\partial^3 \ln Q_x}{\partial \xi^3} = \sum_i \frac{2v_i^4}{n_i^3} - \frac{2}{n^3} \left(\sum_i v_i \right)^4 = \frac{2}{n^3} \left[\sum_i \frac{v_i^4}{x_i^3} - \left(\sum_i v_i \right)^4 \right] \tag{28}$$

or

$$\frac{n^3}{2} \frac{\partial^3 \ln Q_x}{\partial \xi^3} = \sum_i x_i \left[\frac{v_i^2}{x_i^2} - \left(\sum_i v_i \right)^2 \right]^2 + 2 \left(\sum_i v_i \right)^2 \sum_i \frac{1}{x_i} \left(v_i - x_i \sum_i v_i \right)^2 > 0. \tag{29}$$

Thus we have proved that $\partial^2 \ln Q_x/\partial \xi^2$ monotonously increases with ξ. Define

$$g(x_1, x_2, \dots, x_k) = \sum_{i=1}^{k} \frac{v_i^4}{x_i^3} - \left(\sum_{i=1}^{k} v_i \right)^4. \tag{30}$$

By before-mentioned method we can also prove that on the right-hand side of equation (28) is greater than 0, viz. g has the only and positive minimum:

$$g_{\min} = \left(\sum_{i=1}^{k} |v_i| \right)^4 - \left(\sum_{i=1}^{k} v_i \right)^4 = \left[\left(\sum_{i=1}^{k} |v_i| \right)^2 + \left(\sum_{i=1}^{k} v_i \right)^2 \right] f_{\min} > 0. \tag{31}$$

According to above mathematical analysis, we can draw the curve $\ln Q_x - \xi$ (see figure 1). The horizontal line in figure.1 is the curve $\ln K_x - \xi$. In figure 1 we suppose that $\ln K_x > 0$ and

$$\ln Q_x^0 = \sum_i v_i \ln x_i^0 > 0. \tag{32}$$

The point of intersection of the curve $\ln Q_x - \xi$ and the horizontal line $\ln K_x - \xi$ is just the equilibrium point of reaction ξ_e, viz. the only root of equation (1). By equations (5) and (6), we know that if the initial mole number of a certain or some reactants or resultants are 0, then asymptote $\xi = \xi_{\infty,+}$ or $\xi = \xi_{\infty,-}$ will coincide with ordinate axis. By figure 1 we know that equation (1) is fit for finding solution by dichotomy.
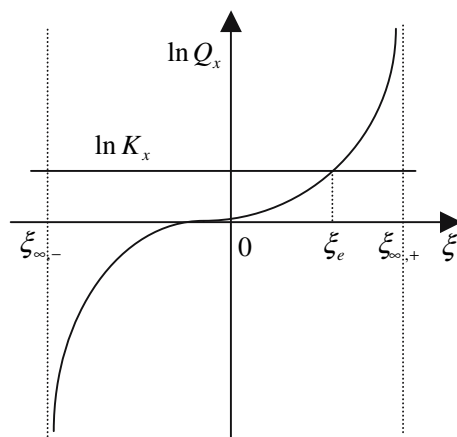
Figure 1. $\ln Q_x$ changes with the extent of reaction ξ.

3. The influence of the temperature and pressure on equilibrium

Owing to

$$\left(\frac{\partial \ln K_x}{\partial T}\right)_p = \frac{\Delta H}{RT^2}, \qquad \left(\frac{\partial \ln K_x}{\partial p}\right)_T = -\frac{\Delta V}{RT}. \tag{33}$$

By equation (33) we know that for the endothermic reaction and the reaction of volume decreasing, to increase temperature and pressure will make the horizontal line in figure 1 shift upwards, but the curve $\ln Q_x - \xi$ does not change with T and p, thus ξ_e increases, equilibrium shift rightwards. Contrarily, for the exothermic reaction and the reaction of volume increasing, to increase temperature and pressure will make equilibrium shift leftwards.

4. The influence of substance on equilibrium

Now we discuss the influence of substance on equilibrium. If we change the initial mole number of substance n_i^0 under isothermal and isobaric condition, the curve $\ln Q_x - \xi$ in figure 1 will shift, thus ξ_e will shift with it. By equation (7) we obtain

$$d \ln Q_x = \sum_i \nu_i d \ln x_i, \tag{34}$$

when ξ is definite, differentiating equation (3), we obtain

$$d \ln x_i = \frac{dn_i^0}{n_i} - \frac{dn^0}{n}. \tag{35}$$

Substituting equation (35) into equation (34), we obtain

$$d \ln Q_x = \sum_i \left(\frac{v_i}{n_i} - \frac{1}{n} \sum_i v_i \right) dn_i^0 \tag{36}$$

by equation (36), we obtain

$$\frac{\partial \ln Q_x}{\partial n_i^0} = \frac{1}{n x_i} \left(v_i - x_i \sum_i v_i \right). \tag{37}$$

Due to

$$v_i - x_i \sum_i v_i = v_i - \frac{n_i^0 + v_i \xi}{n^0 + \xi \sum_i v_i} \sum_i v_i = \frac{n^0}{n} \left(v_i - x_i^0 \sum_i v_i \right). \tag{38}$$

Substituting equation (38) into (37), we obtain

$$\frac{\partial \ln Q_x}{\partial n_i^0} = \frac{n^0}{n^2 x_i} \left(v_i - x_i^0 \sum_i v_i \right). \tag{39}$$

4.1. The influence of the inert substance on equilibrium

If $v_i = 0$, viz. substance i is inert gases, equation (39) becomes

$$\frac{\partial \ln Q_x}{\partial n_i^0} = -\frac{n^0 x_i^0}{n^2 x_i} \sum_i v_i \tag{40}$$

by equation (40) we know that if $\sum_i v_i < 0$, then $\partial \ln Q_x / \partial n_i^0 > 0$, viz. to increase inert gases will make the curve $\ln Q_x - \xi$ in figure 1 shift upwards, ξ_e descends, the equilibrium shifts leftwards; if $\sum_i v_i > 0$, to increase inert gases will make equilibrium shift rightwards; if $\sum_i v_i = 0$, to increase inert gases can not make equilibrium shift.

4.2. The influence of the non-inert substance on equilibrium

Supposing $\sum_i v_i \neq 0$, equation (39) can be rewritten as:

$$\frac{\partial \ln Q_x}{\partial n_i^0} = \frac{n^0}{n^2 x_i v_i^2} \left(\sum_i v_i \right)^2 \frac{v_i}{\sum\limits_i v_i} \left(\frac{v_i}{\sum\limits_i v_i} - x_i^0 \right) v_i, \tag{41}$$

when

$$\frac{v_i}{\sum\limits_i v_i} \left(\frac{v_i}{\sum\limits_i v_i} - x_i^0 \right) > 0 \tag{42}$$

by equation (41) and equation (42) we know that if substance i is reactant, then $v_i < 0$, $\partial \ln Q_x / \partial n_i^0 < 0$, viz. when reactant i increases, the curve $\ln Q_x - \xi$ shifts downwards, ξ_e increases, the equilibrium shifts rightwards; if substance i is resultant, then to increase resultant i will make equilibrium shift leftwards.

The solution of inequality (42) is

$$\frac{v_i}{\sum\limits_i v_i} < 0 \quad \text{or} \quad \frac{v_i}{\sum\limits_i v_i} > x_i^0. \tag{43}$$

So if equation (43) is met, to increase substance i will make equilibrium shift in the direction to deplete substance i.

When

$$\frac{v_i}{\sum\limits_i v_i} \left(\frac{v_i}{\sum\limits_i v_i} - x_i^0 \right) < 0 \tag{44}$$

by equations (41) and (44) we know that if substance i is reactant, viz. $v_i < 0$, then $\partial \ln Q_x / \partial n_i^0 > 0$, viz. when reactant i increase, the curve $\ln Q_x - \xi$ shifts upwards, ξ_e decreases, the equilibrium shift leftwards; if substance i is resultant, then to increase resultant i will make equilibrium shift rightwards.

The solution of inequality (44) is
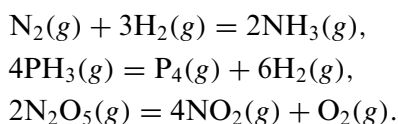
$$x_i^0 > \frac{v_i}{\sum\limits_i v_i} > 0. \tag{45}$$

So if equation (45) is met, to increase substance i will make equilibrium shift in the direction to produce more substance i. This is an amazing result.

Apparently $\sum_i v_i = 0$ is contained in equation (43), because when $\sum_i v_i = 0$, if $v_i < 0$, then $\frac{v_i}{\sum_i v_i} \to -\infty$; if $v_i > 0$, then $\frac{v_i}{\sum_i v_i} \to +\infty$.

The influence of the non-inert substance on equilibrium can be shown by figure 2.

If the non-inert substances changed are the substances with minimal $n_i^0 / |v_i|$, then asymptote in figure 1 will shift, but this does not affect above conclusions.

For following reaction

$$N_2(g) + 3H_2(g) = 2NH_3(g),$$
$$4PH_3(g) = P_4(g) + 6H_2(g),$$
$$2N_2O_5(g) = 4NO_2(g) + O_2(g).$$

$$\frac{v_i}{\sum_i v_i} < 0 \qquad x_i^0 > \frac{v_i}{\sum_i v_i} > 0 \qquad \frac{v_i}{\sum_i v_i} > x_i^0$$

to increase substance i will make equilibrium shift in the direction to deplete substance i.

to increase substance i will make equilibrium shift in the direction to produce more substance i.

to increase substance i will make equilibrium shift in the direction to deplete substance i.
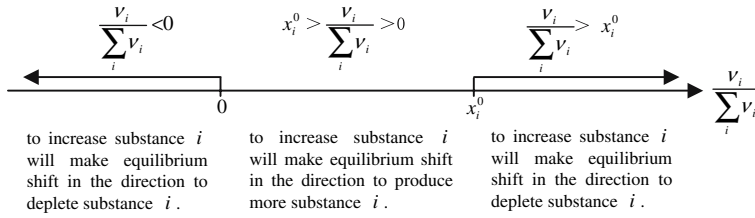
Figure 2. Influence of non-inert substance on equilibrium.

Some substances among them possibly meet $x_i^0 > (v_i / \sum_i v_i) > 0$. For example

$$\frac{v_{N_2}}{\sum_i v_i} = \frac{-1}{-2} = \frac{1}{2} > 0 \qquad \frac{v_{P_4}}{\sum_i v_i} = \frac{1}{3} > 0 \qquad \frac{v_{O_2}}{\sum_i v_i} = \frac{1}{3} > 0.$$

If $x_{N_2}^0 > 1/2$ or $x_{P_4}^0 > 1/3$ or $x_{O_2}^0 > 1/3$, then when N_2 or P_4 or O_2 increases, respectively, the equilibrium will shift in the direction to produce more N_2 or P_4 or O_2, respectively.

5. The change of *Gibbs* free energy of the system with the extent of reaction

Now we discuss the change of *Gibbs* free energy of the system with the extent of reaction. Owing to

$$G = \sum_i n_i \mu_i = \sum_i n_i \mu_i^* + RT \sum_i n_i \ln x_i = \sum_i n_i^0 \mu_i^* + \sum_i v_i \mu_i^* \xi + nRT \sum_i x_i \ln x_i. \tag{46}$$

The first term on the right-hand side of equation (46) is constant during the process of the isothermal and isobaric reactions, for briefness we might as well regard it as 0, thus

$$G = \xi \sum_i v_i \mu_i^* + nRT \sum_i x_i \ln x_i. \tag{47}$$

Substituting equation (1) into equation (47), we obtain

$$G = -\xi \cdot RT \ln K_x + nRT \sum_i x_i \ln x_i, \tag{48}$$

when $x_i \to 0$, $x_i \ln x_i \to 0$, so whether x_i is 0 or not, G is always limited. Owing to

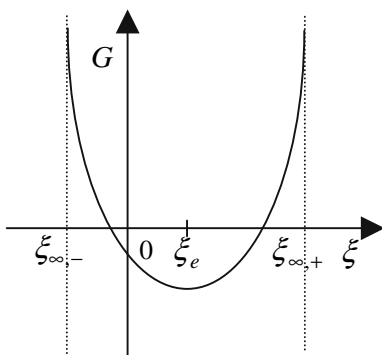$$\left(\frac{\partial G}{\partial \xi} \right)_{T,p} = \Delta G^* + RT \ln Q_x, \tag{49}$$

Figure 3. The change of *Gibbs* free energy of the system with the extent of reaction

when the reactant reacts to the end rightward, $x_r^\# \to 0$, by equations (49) and (7), we know that $(\partial G/\partial \xi)_{T,p} \to +\infty$; when the resultant reacts to the end leftward, $x_p^\# \to 0$, by equations (49) and (8), we know that $(\partial G/\partial \xi)_{T,p} \to -\infty$. Let $(\partial G/\partial \xi)_{T,p}$ in equation (49) vanish, we obtain equation (1); by figure 1 we know that equation (1) has one root ξ_e, viz. G has one extremum point. By equation (49), we obtain

$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,p} = RT \frac{\partial \ln Q_x}{\partial \xi} \tag{50}$$

by equations (12) and (50) we know that, ξ_e is the minimal point of G, and G has no inflexion. By equation (48), we obtain

$$G(0) = n^0 RT \sum_i x_i^0 \ln x_i^0 < 0. \tag{51}$$

Supposing $\xi_e > 0$, we obtain the curve $G - \xi$ shown by figure 3.

6. Conclusion

(1) The curve $\ln Q_x \left(= \sum_i \nu_i \ln x_i\right) - \xi$ is similar to the curve of tangential function which has one inflection and two vertical asymptotes.

(2) The equation $\Delta G^* = -RT \ln Q_x$ only has one root ξ_e and it is suitable to find ξ_e by dichotomy.

(3) For non-inert substance, when $\nu_i / \sum_i \nu_i < 0$ or $\nu_i / \sum_i \nu_i > x_i^0$, to increase substance i will make an equilibrium shift in the direction to deplete substance i; when $x_i^0 > \nu_i / \sum_i \nu_i > 0$, to increase substance i will make an equilibrium shift in the direction to produce more substance i.

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