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A Generalized Formula to Predict the Direction of an Equilibrium Shift

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A generalized formula to predict the direction of an equilibrium shift, $\frac{\partial^2 f}{\partial \xi^2}\frac{\partial \xi}{\partial t}\frac{\partial}{\partial \xi}\left(\frac{\partial f}{\partial t}\right) < 0$, is presented, where ξ is the extent of the reaction, t is the characteristic variable to affect an equilibrium and f is the characteristic function whose partial differential with respect to ξ can be used as an equilibrium criterion. When the stable equilibrium of a thermodynamic system is disturbed on condition that f exhibits a minimum with respect to ξ, the equilibrium will shift in the direction to resist the increase of f if the disturbance make f increase; however, the equilibrium will shift in the direction to accelerate the decrease of f if the disturbance make f decrease to minimize f. On condition that f exhibits a maximum with respect to ξ, the equilibrium will shift in the direction to resist the decrease of f if the disturbance make f decrease; however, the equilibrium will shift in the direction to accelerate the increase of f if the disturbance make f increase to maximize f. On the other hand, Le Chatalier's Principle is not consistent with the real situations under certain circumstances.

KEY WORDS: equilibrium shift, Le Chatalier's principle, generalized formula

1. Introduction

The general principle governing all changes and their affects is Le Chatalier's Principle: if a change of conditions (stress) is applied to an equilibrium system, the system will respond to reduce the stress. But the principle is not consistent with the real situations under certain circumstances. Thus author educes a generalized formula predicting the direction of an equilibrium shift according to the character of characteristic function in thermodynamics.

2. The formulae to predict the direction of equilibrium shift for several particular cases

2.1. *The case for isothermal and isobaric reaction*

In homogeneous system with k components, when a chemical reaction is at equilibrium on isothermal and isobaric condition, the partial differential of

Gibbs free energy G with respect to ξ is equal to 0, viz. $\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = 0$; when the equilibrium shifts, $\mathrm{d}\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = 0$, viz.

$$\mathrm{d}\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial \xi}\right)_{T,p}\right]_p \mathrm{d}T + \left[\frac{\partial}{\partial p}\left(\frac{\partial G}{\partial \xi}\right)_{T,p}\right]_T \mathrm{d}p + \sum_i \left[\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial \xi}\right)_{T,p}\right]_{T,p,n_j} \mathrm{d}n_i = 0 \tag{1}$$

Changing the order of the partial differential in equation (1), we obtain

$$\mathrm{d}\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \left[\frac{\partial}{\partial \xi}\left(\frac{\partial G}{\partial T}\right)_p\right]_{T,p} \mathrm{d}T + \left[\frac{\partial}{\partial \xi}\left(\frac{\partial G}{\partial p}\right)_T\right]_{T,p} \mathrm{d}p + \sum_i \left[\frac{\partial}{\partial \xi}\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j}\right]_{T,p} \mathrm{d}n_i = 0$$

viz.

$$-\left(\frac{\partial S}{\partial \xi}\right)_{T,p} \mathrm{d}T + \left(\frac{\partial V}{\partial \xi}\right)_{T,p} \mathrm{d}p + \sum_i \left(\frac{\partial \mu_i}{\partial \xi}\right)_{T,p} \mathrm{d}n_i = 0. \tag{2}$$

Owing to

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \left(\frac{\partial H}{\partial \xi}\right)_{T,p} - T\left(\frac{\partial S}{\partial \xi}\right)_{T,p} = 0 \tag{3}$$

at equilibrium, so by equation (3), equation (2) can be rewritten as

$$-\frac{1}{T}\left(\frac{\partial H}{\partial \xi}\right)_{T,p} \mathrm{d}T + \left(\frac{\partial V}{\partial \xi}\right)_{T,p} \mathrm{d}p + \sum_i \left(\frac{\partial \mu_i}{\partial \xi}\right)_{T,p} (\mathrm{d}n_i^0 + \nu_i \mathrm{d}\xi) = 0$$

viz.

$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,p} \mathrm{d}\xi = \frac{\Delta H}{T}\mathrm{d}T - \Delta V \mathrm{d}p - \sum_i \Delta\mu_i \mathrm{d}n_i^0, \tag{4}$$

where $\Delta H = \left(\frac{\partial H}{\partial \xi}\right)_{T,p}$ is heat of reaction at isothermal and isobaric condition, $\Delta V = \left(\frac{\partial V}{\partial \xi}\right)_{T,p}$ is the change of volume; $\Delta\mu_i = \left(\frac{\partial \mu_i}{\partial \xi}\right)_{T,p}$ is the change of chemical potential. From equation (4) we obtain

$$\left(\frac{\partial \xi}{\partial T}\right)_p = \frac{\Delta H}{T} \bigg/ \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,p}, \tag{5}$$

$$\left(\frac{\partial \xi}{\partial p}\right)_T = -\Delta V \bigg/ \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,p}, \tag{6}$$

$$\left(\frac{\partial \xi}{\partial n_i^0}\right)_{T,p,n_j^0} = -\Delta \mu_i \bigg/ \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,p}. \tag{7}$$

If the equilibrium is stable, *Gibbs* free energy G exhibits a minimum with respect to ξ at equilibrium, viz. $\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,p} > 0$. Thus by equations (5)–(7) we know that an equilibrium will shift in the direction the reaction is endothermic when temperature increases, in the direction the volume is reductive when pressure increases and in the direction the chemical potential of substance i is descendent when substance i increases.

Above the direction of the equilibrium shift may be expressed by a set of inequality. Two side of equation (5) multiplied by ΔH is

$$\left(\frac{\partial \xi}{\partial T}\right)_p \Delta H > 0 \quad \text{or} \quad -\left(\frac{\partial \xi}{\partial T}\right)_p \Delta S < 0 \tag{8}$$

Analogously

$$\left(\frac{\partial \xi}{\partial p}\right)_T \Delta V < 0 \qquad \left(\frac{\partial \xi}{\partial n_i^0}\right)_{T,p,n_j^0} \Delta \mu_i < 0. \tag{9}$$

Let t_n denote variable T, p and $n_i^0 (i = 1, 2, \dots, k)$, then the second formula in equations (8) and (9) can be rewritten as together expressions:

$$\frac{\partial \xi}{\partial t_n} \frac{\partial \Delta G}{\partial t_n} < 0, \tag{10}$$

where $\Delta G = \left(\frac{\partial G}{\partial \xi}\right)_{T,p}$. The physical meaning of equation (10) can be understood like this: let t_n increase $\partial t_n > 0$, if an equilibrium shift rightward, viz. $\partial \xi > 0$, then $\frac{\partial \Delta G}{\partial t_n} < 0$, viz. $\partial(\Delta G) < 0$, or $\partial(\Delta G) = (\Delta G)_2 - (\Delta G)_1 = (\Delta G)_2 - 0 = (\Delta G)_2 < 0$. The meaning of this result is very obvious, because when $\left(\frac{\partial G}{\partial \xi}\right)_{T,p} < 0$, an equilibrium shift rightward.

Equation (10) can be also rewritten as

$$\frac{\partial \xi}{\partial t_n} \left[\frac{\partial}{\partial \xi}\left(\frac{\partial G}{\partial t_n}\right)\right]_{T,p} < 0. \tag{11}$$

By equation (11) we know that an equilibrium will shift in the direction the change rate of G with respect to t_n decreases when t_n increases. This is intelligible. If the change rate of G with respect to t_n is positive, the decrease of the change rate of G with respect to t_n may make the increase of G with respect to t_n less, viz. the increase of G is resisted; if the change rate of G with respect to t_n is negative, the decrease of the change rate of G with respect to t_n may make the decrease of G with respect to t_n more, viz. the decrease of G is accelerated to minimize G.

Equation (11) indicate that when an chemical equilibrium is disturbed, the system always attempt to minimize G, namely an equilibrium will shift in the direction the increase of G is resisted if the disturbance make G increase; or an equilibrium will shift in the direction the decrease of G is accelerated if the disturbance make G decrease.

The conclusion of equation (10) may also obtained from another angle. Due to

$$\begin{aligned} \mathrm{d}G &= -S\,\mathrm{d}T + V\,\mathrm{d}p + \sum_i \mu_i \mathrm{d}n_i \\ &= -S\,\mathrm{d}T + V\,\mathrm{d}p + \sum_i \mu_i \mathrm{d}\left(n_i^0 + \nu_i \xi\right) \\ &= -S\,\mathrm{d}T + V\mathrm{d}p + \sum_i \mu_i \mathrm{d}n_i^0 + \sum_i \mu_i \nu_i \mathrm{d}\xi \end{aligned} \tag{12}$$

and $\sum_i \mu_i \nu_i = 0$ at equilibrium, so equation (12) becomes

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \sum_i \mu_i \mathrm{d}n_i^0. \tag{13}$$

From equation (13) we obtain

$$\left(\frac{\partial G}{\partial T}\right)_{p,n_1^0,n_2^0,\ldots} = -S, \quad \left(\frac{\partial G}{\partial p}\right)_{T,n_1^0,n_2^0,\ldots} = V, \quad \left(\frac{\partial G}{\partial n_i^0}\right)_{T,p,n_j^0} = \mu_i. \tag{14}$$

Although absolute value of S is unknown, by the first formula in equation (14) we may confirm that the larger algebraic value of S is the better to make *Gibbs* free energy of the system as small as possible. Because when temperature increases, the larger S is, the more *Gibbs* free energy decreases if $S > 0$; or the less *Gibbs* free energy increases if $S < 0$. Thus the equilibrium will shift in the direction S is increscent when temperature increases. The direction S is increscent is the direction the reaction is endothermic. Thus an equilibrium will shift in the direction the reaction is endothermic when temperature increases. By the second formula in equation (14) we know that the smaller V is, the less *Gibbs* free energy increases when pressure increases. Thus an equilibrium will shift in the direction volume is reductive when pressure increases. By the third formula in equation (14) we know that the smaller algebraic value of μ_i is, the less *Gibbs* free energy increases when n_i^0 increases. So an equilibrium will shift in the direction the chemical potential of substance i is descendent when substance i increase.

2.2. The case for isothermal and isochoric reaction

In homogeneous system with k components, when a chemical reaction is at equilibrium on isothermal and isochoric condition, the partial differential of *Helmholz* free energy F with respect to ξ is equal to 0, viz. $\left(\frac{\partial F}{\partial \xi}\right)_{T,V} = 0$; when an equilibrium shift, $\mathrm{d}\left(\frac{\partial F}{\partial \xi}\right)_{T,V} = 0$, viz.

$$\begin{aligned}\mathrm{d}\left(\frac{\partial F}{\partial \xi}\right)_{T,V} = \left[\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial \xi}\right)_{T,V}\right]_V \mathrm{d}T + \left[\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial \xi}\right)_{T,V}\right]_T \mathrm{d}V \\ +\sum_i \left[\frac{\partial}{\partial n_i}\left(\frac{\partial F}{\partial \xi}\right)_{T,V}\right]_{T,V,n_j} \mathrm{d}n_i = 0. \qquad (15)\end{aligned}$$

Analogously we obtain

$$\left(\frac{\partial^2 F}{\partial \xi^2}\right)_{T,V} \mathrm{d}\xi = \frac{\Delta U}{T}\mathrm{d}T + \Delta p\,\mathrm{d}V - \sum_i \Delta\mu_i \mathrm{d}n_i^0, \qquad (16)$$

where $\Delta U = \left(\frac{\partial U}{\partial \xi}\right)_{T,V}$ is heat of reaction at isothermal and isochoric condition, $\Delta p = \left(\frac{\partial p}{\partial \xi}\right)_{T,V}$ is the change of the pressure; $\Delta\mu_i = \left(\frac{\partial \mu_i}{\partial \xi}\right)_{T,V}$ is the change of chemical potential. From equation (16) we obtain

$$\left(\frac{\partial \xi}{\partial T}\right)_V = \frac{\Delta U}{T} \Big/ \left(\frac{\partial^2 F}{\partial \xi^2}\right)_{T,V}, \qquad (17)$$

$$\left(\frac{\partial \xi}{\partial V}\right)_T = \Delta p \Big/ \left(\frac{\partial^2 F}{\partial \xi^2}\right)_{T,V}, \qquad (18)$$

$$\left(\frac{\partial \xi}{\partial n_i^0}\right)_{T,V,n_j^0} = -\Delta\mu_i \Big/ \left(\frac{\partial^2 F}{\partial \xi^2}\right)_{T,V}. \qquad (19)$$

If the equilibrium is stable, *Helmholz* free energy F exhibits a minimum with respect to ξ at equilibrium, viz. $\left(\frac{\partial^2 F}{\partial \xi^2}\right)_{T,V} > 0$. Thus by equations (17)–(19) we know that an equilibrium will shift in the direction reaction is endothermic when temperature increases, in the direction pressure is increscent when volume increases and in the direction chemical potential of substance i is descendent when substance i increases.

Above the direction of the equilibrium shift may be also expressed by a set of inequality:

$$-\left(\frac{\partial\xi}{\partial T}\right)_V \Delta S < 0, \quad -\left(\frac{\partial\xi}{\partial V}\right)_T \Delta p < 0, \quad \left(\frac{\partial\xi}{\partial n_i^0}\right)_{T,V,n_j^0} \Delta\mu_i < 0. \tag{20}$$

Let t_n denote variable T, V and $n_i^0 (i = 1, 2, \ldots, k)$, then equation (20) can be also rewritten as together expressions:

$$\frac{\partial\xi}{\partial t_n}\frac{\partial\Delta F}{\partial t_n} < 0, \tag{21}$$

where $\Delta F = \left(\frac{\partial F}{\partial\xi}\right)_{T,V}$. Equation (21) can be also rewritten as

$$\frac{\partial\xi}{\partial t_n}\left[\frac{\partial}{\partial\xi}\left(\frac{\partial F}{\partial t_n}\right)\right]_{T,V} < 0. \tag{22}$$

We may also discuss equation (22) as if we discussed equation (11).

The conclusions deduced from equation (21) may be also obtained from another angle. Due to

$$\begin{aligned} \mathrm{d}F &= -S\,\mathrm{d}T - p\,\mathrm{d}V + \sum_i \mu_i \mathrm{d}n_i \\ &= -S\,\mathrm{d}T - p\,\mathrm{d}V + \sum_i \mu_i \mathrm{d}\big(n_i^0 + \nu_i\xi\big) \\ &= -S\,\mathrm{d}T - p\,\mathrm{d}V + \sum_i \mu_i \mathrm{d}n_i^0 + \sum_i \mu_i\nu_i \mathrm{d}\xi \end{aligned} \tag{23}$$

and $\sum_i \mu_i\nu_i = 0$ at equilibrium, so equation (23) becomes

$$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \sum_i \mu_i \mathrm{d}n_i^0. \tag{24}$$

From equation (24) we obtain

$$\left(\frac{\partial F}{\partial T}\right)_{V,n_1^0,n_2^0,\ldots} = -S, \quad \left(\frac{\partial F}{\partial V}\right)_{T,n_1^0,n_2^0,\ldots} = -p, \quad \left(\frac{\partial F}{\partial n_i^0}\right)_{T,V,n_j^0} = \mu_i. \tag{25}$$

We may also discuss equation (25) as if we discussed equation (14).

3. The formula to predict the direction of equilibrium shift for generalized cases

Now we educe generalized form of equations (11) and (22). Supposing the characteristic function f, whose partial differential with respect to ξ can be used as an equilibrium criterion, can be shown as

$$f = f(t_1, t_2, \ldots, t_n, \ldots, \xi) \tag{26}$$

where $t_1, t_2, \ldots, t_n, \ldots$, which are characteristic variable to affect an equilibrium, are regarded as parameters and ξ, which is the extent of the reaction, is regarded as variable. f has extreme value with respect to ξ at equilibrium, viz.

$$\frac{\partial f}{\partial \xi} = g(t_1, t_2, \ldots, t_n, \ldots, \xi) = 0. \tag{27}$$

The extreme point ξ is able to be found by equation (27):

$$\xi = \xi(t_1, t_2, \ldots, t_n, \ldots). \tag{28}$$

Now we investigate the influence of parameters $t_1, t_2, \ldots, t_n, \ldots$ on the extreme point of f. Therefore, differentiating equation (26) we obtain

$$\frac{\partial f}{\partial t_n} = \left(\frac{\partial f}{\partial t_n}\right)_\xi + \frac{\partial f}{\partial \xi}\frac{\partial \xi}{\partial t_n}. \tag{29}$$

Substituting equation (27) into (29) we obtain

$$\frac{\partial f}{\partial t_n} = \left(\frac{\partial f}{\partial t_n}\right)_\xi. \tag{30}$$

Differentiating equation (27) we obtain

$$\mathrm{d}\frac{\partial f}{\partial \xi} = \sum_n \left(\frac{\partial g}{\partial t_n}\right)_\xi \mathrm{d}t_n + \frac{\partial g}{\partial \xi}\,\mathrm{d}\xi = 0 \tag{31}$$

viz.

$$\frac{\partial g}{\partial \xi}\,\mathrm{d}\xi = -\sum_n \left(\frac{\partial g}{\partial t_n}\right)_\xi \mathrm{d}t_n \quad \text{or} \quad \frac{\partial^2 f}{\partial \xi^2}\mathrm{d}\xi = -\sum_n \frac{\partial^2 f}{\partial t_n \partial \xi}\,\mathrm{d}t_n. \tag{32}$$

From equation (32) we obtain

$$\frac{\partial^2 f}{\partial \xi^2}\frac{\partial \xi}{\partial t_n} = -\frac{\partial^2 f}{\partial t_n \partial \xi}. \tag{33}$$

Two side of equation (33) multiplied by $\frac{\partial^2 f}{\partial t_n \partial \xi}$ is

$$\frac{\partial^2 f}{\partial \xi^2}\frac{\partial \xi}{\partial t_n}\frac{\partial^2 f}{\partial t_n \partial \xi} = -\left(\frac{\partial^2 f}{\partial t_n \partial \xi}\right)^2. \tag{34}$$

We obtain from equation (34)

$$\frac{\partial^2 f}{\partial \xi^2}\frac{\partial \xi}{\partial t_n}\frac{\partial^2 f}{\partial t_n \partial \xi} < 0 \quad \text{or} \quad \frac{\partial^2 f}{\partial \xi^2}\frac{\partial \xi}{\partial t_n}\frac{\partial}{\partial \xi}\left(\frac{\partial f}{\partial t_n}\right)_{\xi} < 0. \tag{35}$$

Substituting equation (30) into equation (35) we obtain

$$\frac{\partial^2 f}{\partial \xi^2}\frac{\partial \xi}{\partial t_n}\frac{\partial}{\partial \xi}\left(\frac{\partial f}{\partial t_n}\right) < 0. \tag{36}$$

This is just the generalized formula to predict the direction of an equilibrium shift. There are two ∂t_n in equation (36), and there are two $\partial \xi$ besides $\partial \xi$ in $\frac{\partial^2 f}{\partial \xi^2}$, hence when a thermodynamic system arrive at the stable equilibrium, if f exhibits a minimum with respect to ξ $\left(\frac{\partial^2 f}{\partial \xi^2} > 0\right)$, then when the equilibrium is disturbed, by equation (36) we always obtain $\partial(\partial f) < 0$ whether the disturbance ∂t_n is positive or negative, and whether the disturbance make the equilibrium shift rightward ($\partial \xi > 0$) or leftward ($\partial \xi < 0$). This means that if the disturbance makes f increase, viz. $\partial f > 0$, the equilibrium will shift in the direction to resist the increase of f; if the disturbance makes f decrease, viz. $\partial f < 0$, the equilibrium will shift in the direction to accelerate the decrease of f to minimize f. For example, *Gibbs* free energy function $G(T, p, \xi, n_1^0, n_2^0, \ldots)$, *Helmholz* free energy function $F(T, V, \xi, n_1^0, n_2^0, \ldots)$, internal energy function $U(S, V, \xi, n_1^0, n_2^0, \ldots)$ and enthalpy function $H(S, p, \xi, n_1^0, n_2^0, \ldots)$ is just such function.

If f exhibits a maximum with respect to ξ $\left(\frac{\partial^2 f}{\partial \xi^2} < 0\right)$, then when the equilibrium is disturbed, by equation (36) we always obtain $\partial(\partial f) > 0$. This means that if the disturbance makes f increase, the equilibrium will shift in the direction to accelerate the increase of f; if the disturbance makes f decrease, the equilibrium will shift in the direction to resist the decrease of f to maximize f. For example, entropy function $S(U, V, \xi, n_1^0, n_2^0, \ldots)$ is just such function.

The part after the first factor in equation (36) relate to the concavity of the curve $f - t_n$, this can be proved as follows: when only t_n changes, we have

$$\mathrm{d}f = \left(\frac{\partial f}{\partial t_n}\right)_{\xi}\mathrm{d}t_n + \frac{\partial f}{\partial \xi}\mathrm{d}\xi. \tag{37}$$

Differentiating equation (37), we obtain

$$\mathrm{d}^2 f = \mathrm{d}\left(\frac{\partial f}{\partial t_n}\right)_{\xi}\mathrm{d}t_n + \mathrm{d}\frac{\partial f}{\partial \xi}\mathrm{d}\xi, \tag{38}$$

$\mathrm{d}\frac{\partial f}{\partial \xi} = 0$ at equilibrium point, so equation (38) becomes

$$\mathrm{d}^2 f = \mathrm{d}\left(\frac{\partial f}{\partial t_n}\right)_{\xi}\mathrm{d}t_n = \left(\frac{\partial^2 f}{\partial t_n^2}\right)_{\xi}\mathrm{d}t_n^2 + \frac{\partial^2 f}{\partial t_n \partial \xi}\mathrm{d}t_n\mathrm{d}\xi. \tag{39}$$

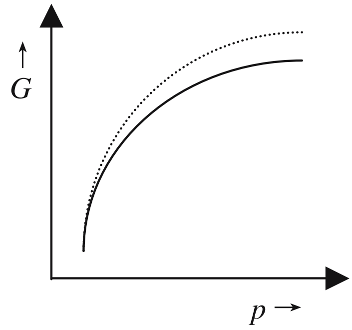

Figure 1. The equilibrium will shift in the direction to resist the increase of *Gibbs* free energy when the pressure increases.

Dividing into equation (39) by $\mathrm{d}t_n^2$, we obtain

$$\frac{\partial^2 f}{\partial t_n^2} = \left(\frac{\partial^2 f}{\partial t_n^2}\right)_\xi + \frac{\partial^2 f}{\partial t_n \partial \xi}\frac{\partial \xi}{\partial t_n} = \left(\frac{\partial^2 f}{\partial t_n^2}\right)_\xi + \frac{\partial \xi}{\partial t_n}\frac{\partial}{\partial \xi}\left(\frac{\partial f}{\partial t_n}\right). \tag{40}$$

The left side of equation (40) denotes the concavity of the curve $f - t_n$ when an equilibrium shifts, the first term on the right of equation (40) denotes the concavity of the curve $f - t_n$ when an equilibrium does not shift, so the second term on the right of equation (40) denotes the influence of an equilibrium shift on the concavity of the curve $f - t_n$. Thus we have proved above proposition.

Now we discuss the change of *Gibbs* free energy with the pressure p when equilibrium does not shift and equilibrium shifts. Due to $\left(\frac{\partial G}{\partial p}\right)_{T,\xi} = V > 0$, $\left(\partial^2 G/\partial p^2\right)_{T,\xi} = (\partial V/\partial p)_{T,\xi} < 0$. So when equilibrium does not shift, the $G - p$ curve can be shown by broken line in figure 1.

If f shows *Gibbs* free energy, t_n shows pressure, then equation (40) becomes

$$\begin{aligned}\left(\frac{\partial^2 G}{\partial p^2}\right)_T &= \left(\frac{\partial^2 G}{\partial p^2}\right)_{T,\xi} + \left(\frac{\partial \xi}{\partial p}\right)_T \frac{\partial}{\partial \xi}\left(\frac{\partial G}{\partial p}\right) \\ &= \left(\frac{\partial^2 G}{\partial p^2}\right)_{T,\xi} + \left(\frac{\partial \xi}{\partial p}\right)_T \left(\frac{\partial V}{\partial \xi}\right)_{T,p}.\end{aligned} \tag{41}$$

Equation (36) becomes

$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,p}\left(\frac{\partial \xi}{\partial p}\right)_T \frac{\partial}{\partial \xi}\left(\frac{\partial G}{\partial p}\right)_T < 0 \quad \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,p}\left(\frac{\partial \xi}{\partial p}\right)_T\left(\frac{\partial V}{\partial \xi}\right)_{T,p} < 0. \tag{42}$$

Owing to $\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,p} > 0$, so by equation (42) we know that the second term on the right of equation (41) $\left(\frac{\partial \xi}{\partial p}\right)_T\left(\frac{\partial V}{\partial \xi}\right)_{T,p} < 0$ [this is actually the first formula in

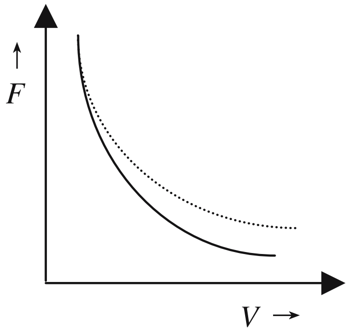

Figure 2. The equilibrium will shift in the direction to accelerate the decrease of *Helmholz* free energy when the volume increases.

equation (9)]. So by equation (41) we know that $\left(\frac{\partial^2 G}{\partial p^2}\right)_T < \left(\frac{\partial^2 G}{\partial p^2}\right)_{T,\xi}$. Again from equation (30) we obtain $\left(\frac{\partial G}{\partial p}\right)_T = \left(\frac{\partial G}{\partial p}\right)_{T,\xi} = V > 0$. So when equilibrium shifts, $G - p$ curve can be shown by the real line in figure 1.

Under definite pressure, the change of *Gibbs* free energy from the broken line to the real line in figure 1 is just the change of *Gibbs* free energy of the system during the process of isothermal and isobaric reaction (it is negative). By figure 1 we know that *Gibbs* free energy of a system increases with the increase of pressure, and the equilibrium shift in the direction to resist the increase of *Gibbs* free energy when the pressure increases.

Now we discuss the change of *Helmholz* free energy with the volume V when equilibrium does not shift and equilibrium shifts. Due to $\left(\frac{\partial F}{\partial V}\right)_{T,\xi} = -p < 0$, $\left(\frac{\partial^2 F}{\partial V^2}\right)_{T,\xi} = -\left(\frac{\partial p}{\partial V}\right)_{T,\xi} > 0$. So when equilibrium does not shift, the $F-V$ curve can be shown by broken line in figure 2.

If f shows *Helmholz* free energy, t_n shows volume, then equation (40) becomes

$$\begin{aligned}\left(\frac{\partial^2 F}{\partial V^2}\right)_T &= \left(\frac{\partial^2 F}{\partial V^2}\right)_{T,\xi} + \left(\frac{\partial \xi}{\partial V}\right)_T \frac{\partial}{\partial \xi}\left(\frac{\partial F}{\partial V}\right) \\ &= \left(\frac{\partial^2 F}{\partial V^2}\right)_{T,\xi} - \left(\frac{\partial \xi}{\partial V}\right)_T \left(\frac{\partial p}{\partial \xi}\right)_{T,V}.\end{aligned} \tag{43}$$

Equation (36) becomes

$$\left(\frac{\partial^2 F}{\partial \xi^2}\right)_{T,V}\left(\frac{\partial \xi}{\partial V}\right)_T \frac{\partial}{\partial \xi}\left(\frac{\partial F}{\partial V}\right)_T < 0 \quad \text{or} \quad \left(\frac{\partial^2 F}{\partial \xi^2}\right)_{T,V}\left(\frac{\partial \xi}{\partial V}\right)_T \left(\frac{\partial p}{\partial \xi}\right)_{T,V} > 0 \tag{44}$$

owing to $\left(\frac{\partial^2 F}{\partial \xi^2}\right)_{T,V} > 0$, so by equation (44) we know that the second term on the right of equation (43) $-\left(\frac{\partial \xi}{\partial V}\right)_T \left(\frac{\partial p}{\partial \xi}\right)_{T,V} < 0$ [this is actually the second formula in equation (20)]. So by equation (43) we know that $\left(\frac{\partial^2 F}{\partial V^2}\right)_T < \left(\frac{\partial^2 F}{\partial V^2}\right)_{T,\xi}$. Again from equation (30) we obtain

$$\left(\frac{\partial F}{\partial V}\right)_T = \left(\frac{\partial F}{\partial V}\right)_{T,\xi} = -p < 0. \tag{45}$$

So when equilibrium shifts, the $F - V$ curve can be shown by the real line in figure 2.

Under definite volume, the change of *Helmholz* free energy from the broken line to the real line in figure 1 is just the change of *Helmholz* free energy of the system during the process of isothermal and isochoric reaction (it is negative). By figure 2 we know that *Helmholz* free energy of a system decreases with the increase of volume, and the equilibrium shift in the direction to accelerate the decrease of *Helmholz* free energy when the volume increases.

4. Discussion about Le Chatalier's principle

Now we discuss Le Chatalier's Principle, and examine whether it is consistent with the real situations or not. Le Chatalier's Principle can be narrated as follows:

"If a stress is imposed on a system at equilibrium (change in concentration, change in temperature, change in pressure), the system will attempt to reduce that stress by shifting the reaction"[1].

From before-mentioned discussion we know that after T, p and n_i^0 are changed, if G increases, an equilibrium will shift in the direction to resist the increase of *Gibbs* free energy. This is consistent with Le Chatalier's Principle. If G decreases, an equilibrium will shift in the direction to accelerate the decrease of *Gibbs* free energy. This is not consistent with Le Chatalier's Principle.

When temperature is changed,

$$\mathrm{d}H = C_p \mathrm{d}T + \left(\frac{\partial H}{\partial \xi}\right)_{T,p} \mathrm{d}\xi = C_p \mathrm{d}T + \Delta H \, \mathrm{d}\xi. \tag{46}$$

From the first term on the right of equation (46) we know that when temperature increases, H increases; moreover when temperature increases, an equilibrium will shift in the direction the reaction is endothermic, viz. $\Delta H \, \mathrm{d}\xi > 0$. So when temperature increases, the equilibrium will shift in the direction to accelerate the increase of H. This is not consistent with Le Chatalier's Principle.

When temperature is changed,

$$\mathrm{d}S = \frac{C_p}{T}\mathrm{d}T + \left(\frac{\partial S}{\partial \xi}\right)_{T,p}\mathrm{d}\xi = \frac{C_p}{T}\mathrm{d}T + \frac{\Delta H}{T}\mathrm{d}\xi. \tag{47}$$

So the change of S is not consistent with Le Chatalier's Principle either.

When the pressure is changed,

$$\mathrm{d}V = \left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p + \left(\frac{\partial V}{\partial \xi}\right)_{T,p}\mathrm{d}\xi = \left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p + \Delta V\,\mathrm{d}\xi. \tag{48}$$

Owing to $\left(\frac{\partial V}{\partial p}\right)_T < 0$, so from the first term on the right of equation (48) we know that when the pressure increases, volume decreases; moreover when the pressure increases an equilibrium will shift in the direction the volume is reductive, viz. $\Delta V\,\mathrm{d}\xi < 0$. So when the pressure increases, the equilibrium will shift in the direction to accelerate the decrease of volume. This is not consistent with Le Chatalier's Principle.

When n_i^0 is changed,

$$\begin{aligned}\mathrm{d}\mu_i &= \sum_j \left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,p,n_l}\mathrm{d}n_j = \sum_j \left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,p,n_l}\mathrm{d}\left(n_j^0 + \nu_j \mathrm{d}\xi\right)\\ &= \sum_j \left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,p,n_l}\mathrm{d}n_j^0 + \sum_j \nu_j \left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,p,n_l}\mathrm{d}\xi\\ &= \left(\frac{\partial \mu_i}{\partial n_i}\right)_{T,p,n_l}\mathrm{d}n_i^0 + \sum_j \nu_j \left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,p,n_l}\mathrm{d}\xi\\ &= \left(\frac{\partial \mu_i}{\partial n_i}\right)_{T,p,n_l}\mathrm{d}n_i^0 + \left(\frac{\partial \mu_i}{\partial \xi}\right)_{T,p}\mathrm{d}\xi. \end{aligned} \tag{49}$$

$\left(\frac{\partial \mu_i}{\partial n_i}\right)_{T,p,n_l} > 0$ for stable equilibrium [2]. So from the first term on the right of equation (49) we know that when n_i^0 increases, μ_i increases; moreover when n_i^0 increases, an equilibrium will shift in the direction chemical potential is descendent, viz. $\left(\frac{\partial \mu_i}{\partial \xi}\right)_{T,p}\mathrm{d}\xi < 0$. So when n_i^0 increases, the equilibrium will shift in the direction to resist the increase of μ_i. This is consistent with Le Chatalier's Principle.

An equilibrium will shift in the direction the reaction is endothermic when temperature increases; by equation (46) we know that if there is not the supply of heat, the temperature of a system will decreases: $\mathrm{d}T = -\frac{\Delta H\,\mathrm{d}\xi}{C_p} < 0$. So the change of T is consistent with Le Chatalier's Principle.

An equilibrium will shift in the direction the number of moles is reductive when the pressure increase, viz. $\Delta V\,\mathrm{d}\xi < 0$; by equation (48) we know that if the volume does not change, then the pressure will decrease: $\mathrm{d}p = -\Delta V\,\mathrm{d}\xi \Big/ \left(\frac{\partial V}{\partial p}\right)_T < 0$. So the change of p is consistent with Le Chatalier's Principle.

When n_i^0 increases, if the equilibrium will shift in the direction n_i^0 is consumed (a majority of cases is so), then this is consistent with Le Chatalier's Principle. But under a minority of cases, when n_i^0 increases, the equilibrium will shift in the direction more n_i^0 is produced [3]. This is not consistent with Le Chatalier's Principle.

We can also make analogous discussion for isothermal and isochoric reaction.

Thus it can be seen that Chatalier's Principle is not consistent with the real situations under certain circumstances.

5. Conclusion

5.1.

A generalized formula to predict the direction of an equilibrium shift is $\frac{\partial^2 f}{\partial \xi^2}\frac{\partial \xi}{\partial t}\frac{\partial}{\partial \xi}\left(\frac{\partial f}{\partial t}\right) < 0$, where ξ is the extent of the reaction, t is the characteristic variable to affect an equilibrium and f is the characteristic function whose partial differential with respect to ξ can be used as an equilibrium criterion.

5.2.

When the stable equilibrium of a thermodynamic system is disturbed on condition that f exhibits a minimum with respect to ξ, the equilibrium will shift in the direction to resist the increase of f if the disturbance make f increase; however, the equilibrium will shift in the direction to accelerate the decrease of f if the disturbance make f decrease to minimize f. On condition that f exhibits a maximum with respect to ξ, the equilibrium will shift in the direction to resist the decrease of f if the disturbance make f decrease; however, the equilibrium will shift in the direction to accelerate the increase of f if the disturbance make f increase to maximize f.

5.3.

Le Chatalier's Principle is not consistent with the real situations under certain circumstances.

References

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[2] Zhang Shi Min, Chemistry, 1 (1996) 103–112.
[3] Zhang Shi Min, Chemistry, 4 (2002) 677–678.