

Influence of substance on the equilibrium translation rate for the isothermal and isobaric chemical reactions of ideal gases

Zhang Shimin

College of Chemistry & Chemical Engineering, Central South University Changsha, Hunan, China

Received 2 March 2005

To increase inert substance i will make the equilibrium translation rate α_j of reactant j decrease if $\sum_i v_i < 0$ or increase if $\sum_i v_i > 0$. When $v_i / \sum_i v_i < 0$, or $v_i / \sum_i v_i \geq 1$, to increase non-inert substance i will make α_j increase if i is reactant ($i \neq j$) or decrease if i is resultant. When $x_i^0 = v_i / \sum_i v_i$, α_j has maximum if i is reactant ($i \neq j$) or minimum if i is resultant. If i is reactant, $x_i^0 = v_i / \sum_i v_i > x_r^0 = |v_r| / \sum_r |v_r|$ (x_r^0 is "optimum proportion" of reactant).

KEY WORDS: equilibrium translation rate, ideal gases, isobaric reactions, optimum proportion

May be owing to the complexity of mathematics, the exhaustive and thorough investigation about the influence of substance on the equilibrium translation rate for the isothermal and isobaric chemical reactions of ideal gases is not seen yet. This problem and "optimum proportion" of reactant will be investigated together in this paper [1–3].

The equilibrium translation rate α_j of reactant j is defined as

$$\alpha_j = (n_j^0 - n_j) / n_j^0 = -v_j \xi / n_j^0 = |v_j| \xi / n_j^0. \quad (1)$$

From equation (1), we know that α_j is the intensive property. The intensive property can be expressed as the function of the concentration of substances. Thereinafter, we investigate the influence of substance concentration on the equilibrium translation rate α_j .

For the isothermal and isobaric chemical reactions of ideal gases, equilibrium constant $K_x = \prod_i x_i^{v_i}$, so

$$\ln K_x = \sum_i v_i \ln \frac{n_i^0 + v_i \xi}{\sum_i n_i^0 + \sum_i v_i \xi} = \sum_i v_i \ln \frac{y_i^0 + v_i \xi / n_j^0}{\sum_i y_i^0 + \sum_i v_i \xi / n_j^0}, \quad (2)$$

where

$$y_i^0 = n_i^0/n_j^0 = x_i^0/x_j^0. \quad (3)$$

Apparently $y_j^0 = 1$. Differentiating equation (2), we obtain

$$\begin{aligned} d \ln K_x &= \sum_i v_i \frac{dy_i^0 + v_i d(\xi/n_j^0)}{y_i^0 + v_i \xi/n_j^0} - \sum_i v_i \frac{\sum_i dy_i^0 + \sum_i v_i d(\xi/n_j^0)}{\sum_i y_i^0 + \sum_i v_i \xi/n_j^0}, \\ &= \sum_i \frac{v_i^2 d(\xi/n_j^0)}{y_i^0 + v_i \xi/n_j^0} - \frac{d(\xi/n_j^0)}{\sum_i y_i^0 + \sum_i v_i \xi/n_j^0} \left(\sum_i v_i \right)^2 \\ &\quad + \sum_i \frac{v_i dy_i^0}{y_i^0 + v_i \xi/n_j^0} - \sum_i \frac{dy_i^0}{\sum_i y_i^0 + \sum_i v_i \xi/n_j^0} \sum_i v_i \\ &= \sum_i v_i^2 \frac{n_j^0}{n_i} d\left(\frac{\xi}{n_j^0}\right) - \frac{n_j^0}{n} \left(\sum_i v_i \right)^2 d\left(\frac{\xi}{n_j^0}\right) \\ &\quad + \sum_i v_i n_j^0 dy_i^0/n_i - n_j^0 \sum_i v_i \sum_i dy_i^0/n \\ &= n_j^0 \left[\sum_i \frac{v_i^2}{n_i} - \frac{1}{n} \left(\sum_i v_i \right)^2 \right] d\left(\frac{\xi}{n_j^0}\right) + n_j^0 \sum_i \left(\frac{v_i}{n_i} - \frac{1}{n} \sum_i v_i \right) dy_i^0 \\ &= a^2 \frac{n_j^0}{n} d\left(\frac{\xi}{n_j^0}\right) + \frac{n_j^0}{n} \sum_i \left(v_i - x_i \sum_i v_i \right) \frac{dy_i^0}{x_i}, \end{aligned} \quad (4)$$

where

$$a^2 = \sum_i \frac{v_i^2}{x_i} - \left(\sum_i v_i \right)^2 = \sum_i \frac{1}{x_i} \left(v_i - x_i \sum_i v_i \right)^2 > 0. \quad (5)$$

Due to $d \ln K_x = 0$ under the isothermal and isobaric condition, so equation (4) becomes

$$a^2 d\left(\frac{\xi}{n_j^0}\right) = - \sum_i \left(v_i - x_i \sum_i v_i \right) \frac{dy_i^0}{x_i}. \quad (6)$$

Owing to

$$\begin{aligned} v_i - x_i \sum_i v_i &= v_i - \frac{n_i}{n} \sum_i v_i = v_i - \frac{n_i^0 + v_i \xi}{n^0 + \xi \sum_i v_i} \sum_i v_i \\ &= \frac{n^0 v_i - n_i^0 \sum_i v_i}{n^0 + \xi \sum_i v_i} = \frac{n^0}{n} \left(v_i - x_i^0 \sum_i v_i \right). \end{aligned} \quad (7)$$

Substituting equation (7) into equation (6), we obtain

$$a^2 d \left(\frac{\xi}{n_j^0} \right) = -\frac{n^0}{n} \sum_i \left(v_i - x_i^0 \sum_i v_i \right) \frac{dy_i^0}{x_i}. \quad (8)$$

Substituting equation (1) into equation (8), we obtain

$$a^2 d\alpha_j = -\frac{n^0}{n} |v_j| \sum_i \left(v_i - x_i^0 \sum_i v_i \right) \frac{dy_i^0}{x_i}. \quad (9)$$

This is just the relationship of the equilibrium translation rate α_j of reactant j with substance concentration. From equation (9) we obtain

$$a^2 \frac{\partial \alpha_j}{\partial y_i^0} = -\frac{n^0}{n x_i} |v_j| \left(v_i - x_i^0 \sum_i v_i \right). \quad (10)$$

Equation (10) is discussed as follows:

If $v_i = 0$, viz. substance i is inert gases, then equation (10) becomes

$$a^2 \frac{\partial \alpha_j}{\partial y_i^0} = \frac{n^0 x_i^0}{n x_i} |v_j| \sum_i v_i. \quad (11)$$

Equation (11) shows that if $\sum_i v_i < 0$, then $\frac{\partial \alpha_j}{\partial y_i^0} < 0$, viz. to increase the concentration y_i^0 of inert gases i will make the equilibrium translation rate α_j of reactant j decrease; if $\sum_i v_i > 0$, then $\frac{\partial \alpha_j}{\partial y_i^0} > 0$, viz. to increase the concentration y_i^0 of inert gases i will make the equilibrium translation rate α_j of reactant j increase.

If $v_i \neq 0$, then equation (10) can be rewritten as

$$a^2 \frac{\partial \alpha_j}{\partial y_i^0} = -\frac{n^0 |v_j|}{n x_i v_i^2} \left(\sum_i v_i \right)^2 \frac{v_i}{\sum_i v_i} \left(\frac{v_i}{\sum_i v_i} - x_i^0 \right) v_i. \quad (12)$$

If

$$\frac{v_i}{\sum_i v_i} < 0 \quad \text{or} \quad \frac{v_i}{\sum_i v_i} > 1. \quad (13)$$

From equation (12) we know that when i is reactant, $v_i < 0$, $\frac{\partial \alpha_j}{\partial y_i^0} > 0$, viz. to increase the concentration y_i^0 of reactant i will make the equilibrium translation rate α_j of reactant j ($j \neq i$) increase; when i is resultant, $v_i > 0$, $\frac{\partial \alpha_j}{\partial y_i^0} < 0$, viz. to increase the concentration y_i^0 of resultant i will make the equilibrium translation rate α_j of reactant j decrease. If

$$1 > \frac{v_i}{\sum_i v_i} > 0. \quad (14)$$

From equation (12) we know that when $v_i < 0$, if $x_i^0 < \frac{v_i}{\sum_i v_i}$, $\frac{\partial \alpha_j}{\partial y_i^0} > 0$; if $x_i^0 > \frac{v_i}{\sum_i v_i}$, $\frac{\partial \alpha_j}{\partial y_i^0} < 0$; if

$$x_i^0 = \frac{v_i}{\sum_i v_i} = x_{i,m}^0, \quad (15)$$

$\frac{\partial \alpha_j}{\partial y_i^0} = 0$. So when equation (14) is met and $v_i < 0$, α_j has maximum at $x_{i,m}^0$. Analogously when equation (14) is met and $v_i > 0$, α_j has minimum at $x_{i,m}^0$. Due to

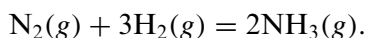
$$y_i^0 = n_i^0/n_j^0 = x_i^0/x_j^0 = x_i^0 / \left(1 - x_i^0 - \sum_{l \neq j,i} x_l^0 \right), \quad (16)$$

so

$$y_{i,m}^0 = x_{i,m}^0 / \left(1 - x_{i,m}^0 - \sum_{l \neq j,i} x_l^0 \right) = \left(v_i / \sum_i v_i \right) / \left(1 - v_i / \sum_i v_i - \sum_{l \neq j,i} x_l^0 \right). \quad (17)$$

When $0 < v_i / \sum_i v_i < 1$, the curves of α_j versus y_i^0 are shown in figure 1. $0 < v_i / \sum_i v_i < x_i^0$ on the right-hand side of the extremum point of the curves in figure 1 and $x_i^0 < v_i / \sum_i v_i < 1$ on the left-hand side of the extremum point of the curves in figure 1. From figure 1, we know that on the right-hand side of the extremum point, the equilibrium translation rate α_j of reactant j decreases with the increase of reactant concentration y_i^0 [see figure 1a] or increase with the increase of resultant concentration y_i^0 [see figure 1b]. This is an abnormal result.

Above discussion can be summarized as follows: to increase the equilibrium translation rate α_j of reactant j , when equation (13) is met, the initial concentration of reactant should be as large as possible, the initial concentration of resultant should be as small as possible; when equation (14) is met, the initial concentration of reactant should adopt the value expressed by equation (15), the initial concentration of resultant should avoid the value expressed by equation (15). For example for the reaction to synthesize ammonia



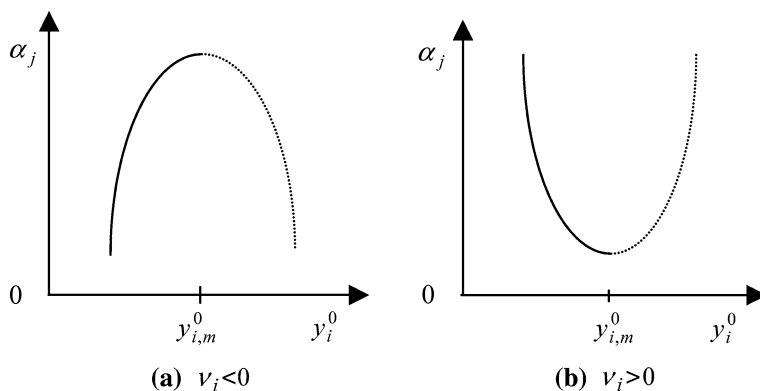
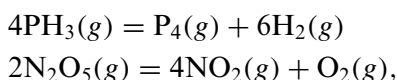


Figure 1. The equilibrium translation rate α_j of reactant j changes with initial mole fraction of non-inert substance y_i^0 ($0 < v_i / \sum_i v_i < 1$) broken line: $0 < v_i / \sum_i v_i < x_i^0$ real line: $x_i^0 < v_i / \sum_i v_i < 1$.

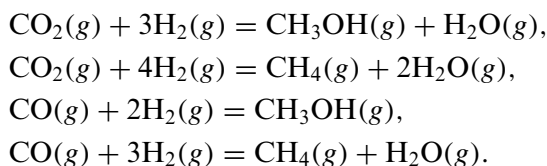
Because $\text{H}_2(\text{g})$ is more expensive than $\text{N}_2(\text{g})$, to increase the equilibrium translation rate of $\text{H}_2(\text{g})$, $x_{\text{N}_2}^0$ should meet equation (15):

$$x_{\text{N}_2}^0 = v_{\text{N}_2} / \sum_i v_i = 1/2.$$

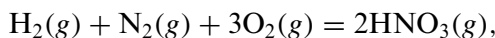
For reaction



to increase the equilibrium translation rate of $\text{PH}_3(\text{g})$, $x_{\text{P}_4}^0$ should avoid $x_{\text{P}_4}^0 = v_{\text{P}_4} / \sum_i v_i = 1/3$; to increase the equilibrium translation rate of $\text{N}_2\text{O}_5(\text{g})$, $x_{\text{O}_2}^0$ should avoid $x_{\text{O}_2}^0 = v_{\text{O}_2} / \sum_i v_i = 1/3$ too. For the following reaction



To increase the equilibrium translation rate of $\text{H}_2(\text{g})$, $x_{\text{CO}_2}^0$ and x_{CO}^0 should meet $x_{\text{CO}_2}^0 = v_{\text{CO}_2} / \sum_i v_i = 1/2$ and $x_{\text{CO}}^0 = v_{\text{CO}} / \sum_i v_i = 1/2$, respectively. For reaction



if we want to increase the equilibrium translation rate of $\text{O}_2(\text{g})$, then $x_{\text{N}_2}^0$ and $x_{\text{H}_2}^0$ should meet $x_{\text{N}_2}^0 = v_{\text{N}_2} / \sum_i v_i = 1/3$ and $x_{\text{H}_2}^0 = v_{\text{H}_2} / \sum_i v_i = 1/3$, respectively.

For $v_i < 0$, equation (15) can be rewritten as

$$x_r^0 = v_r / \sum_i v_i = |v_r| / \left| \sum_i v_i \right|, \quad (18)$$

where subscript r denotes reactant. Owing to $v_r < 0$, $x_i^0 > 0$, so $\sum_i v_i < 0$, viz.

$$\sum_i v_i = \sum_p v_p + \sum_r v_r = \sum_p v_p - \sum_r |v_r| < 0,$$

where subscript p denotes production or resultant. So equation (18) can be rewritten as

$$x_r^0 = |v_r| / \left(\sum_r |v_r| - \sum_p v_p \right). \quad (19)$$

Now we deduce "optimum proportion" of reactant. Supposing that the initial mole fractions of resultants $x_p^0 = 0$, then the equilibrium mole fractions of resultants

$$x_p = \frac{v_p \xi / n^0}{1 + \sum_i v_i \xi / n^0}. \quad (20)$$

Differentiating equation (20), we obtain

$$\begin{aligned} dx_p &= \frac{v_p d(\xi/n^0)}{1 + \sum_i v_i \xi/n^0} - \frac{v_p \xi/n^0}{\left(1 + \sum_i v_i \xi/n^0\right)^2} \sum_i v_i d(\xi/n^0) \\ &= \frac{v_p d(\xi/n^0)}{\left(1 + \sum_i v_i \xi/n^0\right)^2} = \frac{n^{02}}{n^2} v_p d(\xi/n^0). \end{aligned} \quad (21)$$

From equation (2) we obtain

$$\ln K_x = \sum_i v_i \ln (x_i^0 + v_i \xi/n^0) - \sum_i v_i \ln \left(1 + \sum_i v_i \xi/n^0 \right). \quad (22)$$

Differentiating equation (22), we obtain

$$\begin{aligned}
 d \ln K_x &= \sum_i v_i \frac{dx_i^0 + v_i d(\xi/n^0)}{x_i^0 + v_i \xi/n^0} - \left(\sum_i v_i \right)^2 \frac{d(\xi/n^0)}{1 + \sum_i v_i \xi/n^0} \\
 &= \sum_i \frac{v_i dx_i^0}{x_i^0 + v_i \xi/n^0} \\
 &\quad + \left[\sum_i \frac{v_i^2}{x_i^0 + v_i \xi/n^0} - \left(\sum_i v_i \right)^2 / \left(1 + \sum_i v_i \xi/n^0 \right) \right] d \left(\frac{\xi}{n^0} \right) \\
 &= n^0 \sum_i \frac{v_i dx_i^0}{n_i} + n^0 \left[\sum_i \frac{v_i^2}{n_i} - \frac{1}{n} \left(\sum_i v_i \right)^2 \right] d \left(\frac{\xi}{n^0} \right). \tag{23}
 \end{aligned}$$

Due to $d \ln K_x = 0$ under the isothermal and isobaric condition, so equation (23) becomes

$$\left[\sum_i \frac{v_i^2}{x_i} - \left(\sum_i v_i \right)^2 \right] d \left(\frac{\xi}{n^0} \right) = - \sum_i \frac{v_i dx_i^0}{x_i}. \tag{24}$$

Substituting equation (5) into equation (24), and taking note of $x_p^0=0$, we obtain

$$a^2 d \left(\frac{\xi}{n^0} \right) = - \sum_r \frac{v_r dx_r^0}{x_r}. \tag{25}$$

Substituting equation (25) into equation (21), we obtain

$$\begin{aligned}
 a^2 dx_p &= -v_p \frac{n^{02}}{n^2} \sum_r \frac{v_r dx_r^0}{x_r} = -v_p \frac{n^{02}}{n^2} \left(\sum_{r \neq j} \frac{v_r dx_r^0}{x_r} + \frac{v_j dx_j^0}{x_j} \right) \\
 &= -v_p \frac{n^{02}}{n^2} \left(\sum_{r \neq j} \frac{v_r dx_r^0}{x_r} - \frac{v_j}{x_j} \sum_{r \neq j} dx_r^0 \right) = -v_p \frac{n^{02}}{n^2} \sum_{r \neq j} \left(\frac{v_r}{x_r} - \frac{v_j}{x_j} \right) dx_r^0. \tag{26}
 \end{aligned}$$

Due to

$$x_r = \frac{x_r^0 + v_r \xi/n^0}{1 + \sum_i v_i \xi/n^0}, \tag{27}$$

so

$$\frac{x_r}{v_r} = \frac{x_r^0/v_r + \xi/n^0}{1 + \sum_i v_i \xi/n^0} = \frac{n^0}{n} \left(\frac{x_r^0}{v_r} + \frac{\xi}{n^0} \right). \quad (28)$$

From equation (28), we obtain

$$\frac{x_j}{v_j} = \frac{n^0}{n} \left(\frac{x_j^0}{v_j} + \frac{\xi}{n^0} \right). \quad (29)$$

Equation (28) minus equation (29):

$$\frac{x_r}{v_r} - \frac{x_j}{v_j} = \frac{n^0}{n} \left(\frac{x_r^0}{v_r} - \frac{x_j^0}{v_j} \right),$$

or

$$\left(\frac{v_r}{x_r} - \frac{v_j}{x_j} \right) = \frac{n^0 x_r^0 x_j^0}{n x_r x_j} \left(\frac{v_r}{x_r^0} - \frac{v_j}{x_j^0} \right). \quad (30)$$

Substituting equation (30) into equation (26), we obtain

$$a^2 dx_p = -v_p \frac{n^0 x_j^0}{n^3 x_j} \sum_{r \neq j} \frac{x_r^0}{x_r} \left(\frac{v_r}{x_r^0} - \frac{v_j}{x_j^0} \right) dx_r^0, \quad (31)$$

or

$$a^2 \frac{\partial x_p}{\partial x_r^0} = -v_p \frac{n^0 x_j^0 x_r^0}{n^3 x_j x_r} \left(\frac{v_r}{x_r^0} - \frac{v_j}{x_j^0} \right). \quad (32)$$

This is just the relationship of the equilibrium mole fractions of resultants and the initial concentrations of reactants.

For inert gases, $v_r = 0$, equation (32) becomes

$$a^2 \frac{\partial x_p}{\partial x_r^0} = v_p \frac{n^0 v_j x_r^0}{n^3 x_j x_r} < 0, \quad (33)$$

so $\frac{\partial x_p}{\partial x_r^0} < 0$, viz. when the initial concentration of inert gases x_r^0 increases, the equilibrium concentration of resultant x_p decreases.

For non-inert gases, by equation (32) we know that if

$$v_r/x_r^0 = v_j/x_j^0, \quad (34)$$

then $dx_p = 0$, viz. x_p has extremum. Equation (34) can be also rewritten as

$$x_r^0 = v_r x_j^0 / v_j. \quad (35)$$

Finding sum to equation (35), we obtain

$$\sum_r x_r^0 = (x_j^0 / \nu_j) \sum_r \nu_r \quad \text{or} \quad x_j^0 / \nu_j = \sum_r x_r^0 / \sum_r \nu_r. \quad (36)$$

Substituting equation (36) into equation (35), we obtain

$$x_r^0 = \frac{\nu_r}{\sum_r \nu_r} \sum_r x_r^0 = \frac{|\nu_r|}{\sum_r |\nu_r|} \sum_r x_r^0 = x_{r,m}^0. \quad (37)$$

If there are not inert gases, then $\sum_r x_r^0 = 1$, equation (37) becomes

$$x_r^0 = \frac{|\nu_r|}{\sum_r |\nu_r|} = x_{r,m}^0. \quad (38)$$

This is just the extremum point of the equilibrium mole fractions of resultants x_p . It is a maximum point, this can be proved as follows: equation (26) can be rewritten as

$$a^2 \frac{n^2}{n^{02}} dx_p = -\nu_p \sum_r \frac{\nu_r dx_r^0}{x_r}. \quad (39)$$

Differentiating equation (39), we obtain

$$d \left(a^2 \frac{n^2}{n^{02}} \right) dx_p + a^2 \frac{n^2}{n^{02}} d^2 x_p = \nu_p \sum_r \frac{\nu_r dx_r dx_r^0}{(x_r)^2}. \quad (40)$$

Due to $dx_p = 0$ at extremum point, so equation (40) becomes

$$a^2 \frac{n^2}{n^{02}} d^2 x_p = \nu_p \sum_r \frac{\nu_r dx_r dx_r^0}{(x_r)^2}. \quad (41)$$

Differentiating equation (27), we obtain

$$dx_r = \frac{[dx_r^0 + \nu_r d(\xi/n^0)] (1 + \sum_i \nu_i \xi/n^0) - (x_r^0 + \nu_r \xi/n^0) \sum_i \nu_i d(\xi/n^0)}{(1 + \sum_i \nu_i \xi/n^0)^2}. \quad (42)$$

Due to $dx_p = 0$ at extremum point, so from equation (21), we know that $d(\xi/n^0) = 0$ at extremum point. So equation (42) becomes

$$dx_r = \frac{dx_r^0}{1 + \sum_i \nu_i \xi/n^0} = \frac{n^0}{n} dx_r^0. \quad (43)$$

Substituting equation (43) into equation (41), we obtain

$$a^2 \frac{n^3}{n^{03}} d^2 x_p = \nu_p \sum_r \frac{\nu_r (dx_r^0)^2}{(x_r)^2} < 0. \quad (44)$$

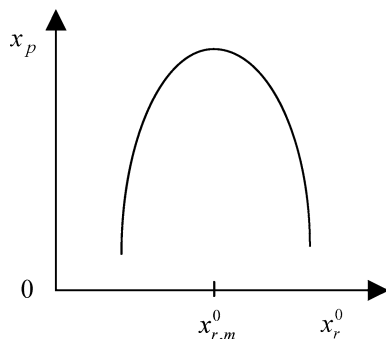


Figure 2. x_p changes with x_r^0 .

So equation (38) is a maximum point. The curve of x_p versus x_r^0 is shown in figure 2.

By equation (19) and equation (38) we know that

$$|v_r| / \left(\sum_r |v_r| - \sum_p v_p \right) > |v_r| / \sum_r |v_r|.$$

For example for the reaction to synthesize ammonia, from equation (19) we obtain $x_{\text{N}_2}^0 = 1/2$; from equation (38) we obtain $x_{\text{N}_2}^0 = 1/4$.

References

- [1] Zhang Shimin, Chemistry, 53(1) (1995) 57–62 (Chinese).
- [2] Zhang Shimin, Chemistry, 54(1) (1996) 97–102 (Chinese).
- [3] Zhang Shimin, J. Math. Chem. 38(2) (2005) 129–140.