

## Review of Chemical Equilibria

### A.1 | Basic Criteria for Chemical Equilibrium of Reacting Systems

The basic criterion for equilibrium with a single reaction is:

$$\Delta G = \sum_{i=1}^{NCOMP} v_i \mu_i = 0 \quad (\text{A.1.1})$$

where  $\Delta G$  is the Gibbs function,  $NCOMP$  is the number of components in the system,  $v_i$  is the stoichiometric coefficient of species  $i$ , and  $\mu_i$  is the chemical potential of species  $i$ . The chemical potential is:

$$\mu_i = \mu_i^0 + R_g T \ln a_i \quad (\text{A.1.2})$$

where  $R_g$  is the universal gas constant,  $\mu_i^0$  is the standard chemical potential of species  $i$  in a reference state such that  $a_i = 1$ , and  $a_i$  is the activity of species  $i$ . The reference states are: (1) for gases (i.e.,  $\bar{f}^0 = 1$ ) (ideal gas,  $P = 1$  atm) where  $\bar{f}$  is the fugacity, (2) for liquids, the pure liquid at  $T$  and one atmosphere, and (3) for solids, the pure solid at  $T$  and one atmosphere. If multiple reactions are occurring in a network, then Equation (A.1.1) can be extended to give:

$$\Delta G_j = \sum_{i=1}^{NCOMP} v_{i,j} \mu_i = 0, \quad j = 1, \dots, NRXN \quad (\text{A.1.3})$$

where  $NRXN$  is the number of independent reactions in the network.

In general it is not true that the change in the standard Gibbs function,  $\Delta G^0$ , is zero. Thus,

$$\Delta G^0 = \sum_{i=1}^{NCOMP} v_i \mu_i^0 \neq 0 \quad (\text{A.1.4})$$

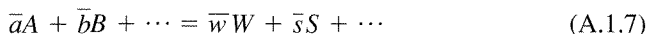
Therefore,

$$\Delta G - \Delta G^0 = \sum_{i=1}^{NCOMP} \nu_i (\mu_i - \mu_i^0) \quad (\text{A.1.5})$$

or by using Equation (A.1.2):

$$\Delta G - \Delta G^0 = R_g T \sum_{i=1}^{NCOMP} \nu_i \ln a_i = R_g T \ln \left( \prod_i a_i^{\nu_i} \right) \quad (\text{A.1.6})$$

Now consider the general reaction:



Application of Equation (A.1.6) to Equation (A.1.7) and recalling that  $\Delta G = 0$  at equilibrium gives:

$$\Delta G^0 = -R_g T \ln \left[ \frac{a_W^{\bar{w}} a_S^{\bar{s}} \cdots}{a_A^{\bar{a}} a_B^{\bar{b}} \cdots} \right] = -R_g T \ln K_a \quad (\text{A.1.8})$$

Thus, the equilibrium constant  $K_a$  is defined as:

$$K_a = \prod_{i=1}^{NCOMP} a_i^{\nu_i} \quad (\text{A.1.9})$$

Differentiation of Equation (A.1.8) with respect to  $T$  yields:

$$\left[ \frac{\partial(\Delta G^0/T)}{\partial T} \right]_P = -R_g \left[ \frac{\partial(\ln K_a)}{\partial T} \right]_P \quad (\text{A.1.10})$$

Note that  $\Delta G^0 = \Delta H^0 - T\Delta S^0$ , where  $\Delta H^0$  and  $\Delta S^0$  are the standard enthalpy and entropy, respectively, and differentiation of this expression with respect to  $T$  gives:

$$\left[ \frac{\partial(\Delta G^0/T)}{\partial T} \right]_P = -\frac{\Delta H^0}{T^2} \quad (\text{A.1.11})$$

Equating Equations (A.1.10) and (A.1.11) provides the functional form for the temperature dependence of the equilibrium constant:

$$\left[ \frac{\partial(\ln K_a)}{\partial T} \right]_P = \frac{\Delta H^0}{R_g T^2} \quad (\text{A.1.12})$$

or after integration (assume  $\Delta H^0$  is independent of  $T$ ):

$$K_a = \bar{K} \exp[-\Delta H^0/(R_g T)] \quad (\text{A.1.13})$$

Notice that when the reaction is exothermic ( $\Delta H^0$  is negative),  $K_a$  increases with decreasing  $T$ . For endothermic reactions the opposite is true. From Equation (A.1.8):

$$\frac{-\Delta G^0}{R_g T} = \ln K_a \quad (\text{A.1.14})$$

and

$$K_a = \exp\left[-\Delta G^0/(R_g T)\right] \quad (\text{A.1.15})$$

Since  $\Delta G^0$  is not a function of pressure, it is clear that pressure has no influence on  $K_a$ .

## A.2 | Determination of Equilibrium Compositions

Consider a gas-phase reaction. If the Lewis and Randall mixing rules are used (simplest form of mixing rules—more sophisticated relationships could be applied if deemed necessary) to give for the fugacity of species  $i$ ,  $\bar{f}_i$ :

$$a = \bar{f}_i/\bar{f}_i^0 \quad (\text{A.2.1})$$

where

$$\bar{f}_i = X_i \bar{\phi}_i P$$

and  $\bar{\phi}_i$  = fugacity coefficient of pure  $i$  at  $T$  and  $P$  of system for any mole fraction  $X_i$ . Substituting the above expression into Equation (A.1.9) for the reaction given in Equation (A.1.7) yields (let all  $\bar{f}_i^0 = 1$ ):

$$K_a = \left[ \frac{X_W^{\bar{w}} X_S^{\bar{s}} \cdots}{X_A^{\bar{a}} X_B^{\bar{b}} \cdots} \right] \left[ \frac{\bar{\phi}_W^{\bar{w}} \bar{\phi}_S^{\bar{s}} \cdots}{\bar{\phi}_A^{\bar{a}} \bar{\phi}_B^{\bar{b}} \cdots} \right] P^{\bar{w} + \bar{s} + \cdots - \bar{a} - \bar{b} \cdots} \quad (\text{A.2.2})$$

or

$$K_a = K_x K_{\bar{\phi}} P^{\bar{w} + \bar{s} + \cdots - \bar{a} - \bar{b} \cdots}$$

where

$$X_i = \frac{n_i}{n_{\text{inert}} + \sum_j n_j}$$

Equation (A.2.2) can be written in terms of moles as:

$$K_a = K_{\bar{\phi}} \left[ \frac{n_W^{\bar{w}} n_S^{\bar{s}} \cdots}{n_A^{\bar{a}} n_B^{\bar{b}} \cdots} \right] \left[ \frac{P}{n_{\text{inert}} + \sum_j n_j} \right]^{\bar{w} + \bar{s} + \cdots - \bar{a} - \bar{b} \cdots} \quad (\text{A.2.3})$$

Note that  $K_a$  is not a function of pressure and that  $K_{\bar{\phi}}$  is only weakly dependent on pressure. Thus, if:

$$\bar{w} + \bar{s} + \cdots - \bar{a} - \bar{b} \cdots = \begin{cases} - & \text{then } P \uparrow, K_x \uparrow \\ + & \text{then } P \uparrow, K_x \downarrow \\ 0 & \text{then no effect} \end{cases}$$

and the effect of inert species are:

$$\bar{w} + \bar{s} + \cdots - \bar{a} - \bar{b} \cdots = \begin{cases} - & \text{then add inert, } K_x \downarrow \\ + & \text{then add inert, } K_x \uparrow \\ 0 & \text{then no effect} \end{cases}$$

Finally, just to state clearly once again, a catalyst has no effect on equilibrium yields.

# Regression Analysis

## B.1 | Method of Least Squares

Below is illustrated the method of least squares to fit a straight line to a set of data points  $(y_i, x_i)$ . Extensions to nonlinear least squares fits are discussed in Section B.4.

Consider the problem of fitting a set of data  $(y_i, x_i)$  where  $y$  and  $x$  are the dependent and independent variables, respectively, to an equation of the form:

$$y = \bar{\alpha}_1 + \bar{\alpha}_2 x \quad (\text{B.1.1})$$

by determining the coefficients  $\bar{\alpha}_1$  and  $\bar{\alpha}_2$  so that the differences between  $y_i$  and  $y_i = \bar{\alpha}_1 + \bar{\alpha}_2 x_i$  are minimized. Given  $\bar{\alpha}_1$  and  $\bar{\alpha}_2$ , the deviations  $\Delta y_i$  can be calculated as:

$$\Delta y_i = y_i - \bar{\alpha}_1 - \bar{\alpha}_2 x_i \quad (\text{B.1.2})$$

For any value of  $x = x_i$ , the probability  $PP_i$  for making the observed measurement  $y_i$  with a Gaussian distribution and a standard deviation  $\sigma_i$  for the observations about the actual value  $y(x_i)$  is (P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill, New York, 1969, p. 101):

$$PP_i = \frac{1}{\sigma_i \sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left[ \frac{y_i - y(x_i)}{\sigma_i} \right]^2 \right] \quad (\text{B.1.3})$$

The probability of making the observed data set of measurements of the  $N$  values of  $y_i$  is the product of the individual  $PP_i$  or:

$$PP(\bar{\alpha}_1, \bar{\alpha}_2) = \prod_i^N PP_i = \prod_i^N \left( \frac{1}{\sigma_i \sqrt{2\pi}} \right) \exp \left[ -\frac{1}{2} \sum_i^N \left[ \frac{y_i - y(x_i)}{\sigma_i} \right]^2 \right] \quad (\text{B.1.4})$$

The best estimates for  $\bar{\alpha}_1$  and  $\bar{\alpha}_2$  are the values that maximize  $PP(\bar{\alpha}_1, \bar{\alpha}_2)$  (method of maximum likelihood). Define:

$$\bar{X}^2 = \sum_i^N \left[ \frac{y_i - y(x_i)}{\sigma_i} \right]^2 = \sum_i^N \left[ \frac{1}{\sigma_i^2} (y_i - \bar{\alpha}_1 - \bar{\alpha}_2 x_i)^2 \right] \quad (\text{B.1.5})$$

Note that in order to maximize  $PP(\bar{\alpha}_1, \bar{\alpha}_2)$ ,  $\bar{X}^2$  is minimized. Thus, the method to find the optimum fit to the data is to minimize the sum of the squares of the deviations (i.e., least-squares fit).

As an example of how to calculate  $\bar{\alpha}_1$  and  $\bar{\alpha}_2$ , consider here the case where  $\sigma_i = \sigma = \text{constant}$ . To minimize  $\bar{X}^2$ , the partial derivatives of  $\bar{X}^2$  with respect to  $\bar{\alpha}_1$  and  $\bar{\alpha}_2$  must be set equal to zero:

$$\begin{aligned} \frac{\partial \bar{X}^2}{\partial \bar{\alpha}_1} &= 0 = \frac{\partial}{\partial \bar{\alpha}_1} \left[ \frac{1}{\sigma^2} \sum (y_i - \bar{\alpha}_1 - \bar{\alpha}_2 x_i)^2 \right] = \frac{-2}{\sigma^2} \sum (y_i - \bar{\alpha}_1 - \bar{\alpha}_2 x_i) \\ \frac{\partial \bar{X}^2}{\partial \bar{\alpha}_2} &= 0 = \frac{\partial}{\partial \bar{\alpha}_2} \left[ \frac{1}{\sigma^2} \sum (y_i - \bar{\alpha}_1 - \bar{\alpha}_2 x_i)^2 \right] = \frac{-2}{\sigma^2} \sum x_i (y_i - \bar{\alpha}_1 - \bar{\alpha}_2 x_i) \end{aligned}$$

These equations can be rearranged to give:

$$\begin{aligned} \sum y_i &= \sum \bar{\alpha}_1 + \sum \bar{\alpha}_2 x_i = \bar{\alpha}_1 N + \bar{\alpha}_2 \sum x_i \\ \sum x_i y_i &= \sum \bar{\alpha}_1 x_i + \sum \bar{\alpha}_2 x_i^2 = \bar{\alpha}_1 \sum x_i + \bar{\alpha}_2 \sum x_i^2 \end{aligned}$$

The solutions to these equations yield  $\bar{\alpha}_1$  and  $\bar{\alpha}_2$  in the following manner:

$$\left. \begin{aligned} \bar{\alpha}_1 &= \frac{\begin{vmatrix} \sum y_i & \sum x_i \\ \sum x_i y_i & \sum x_i^2 \end{vmatrix}}{\begin{vmatrix} N & \sum x_i \\ \sum x_i & \sum x_i^2 \end{vmatrix}} = \frac{\sum y_i \sum x_i^2 - \sum x_i \sum x_i y_i}{N \sum x_i^2 - (\sum x_i)^2} \\ \bar{\alpha}_2 &= \frac{\begin{vmatrix} N & \sum y_i \\ \sum x_i & \sum x_i y_i \end{vmatrix}}{\begin{vmatrix} N & \sum x_i \\ \sum x_i & \sum x_i^2 \end{vmatrix}} = \frac{N \sum x_i y_i - \sum x_i \sum y_i}{N \sum x_i^2 - (\sum x_i)^2} \end{aligned} \right\} \quad (\text{B.1.6})$$

The calculation is straightforward. First compute  $\sum x_i$ ,  $\sum y_i$ ,  $\sum x_i^2$ , and  $\sum x_i y_i$ . Second use the summed values in Equation (B.1.6) to obtain  $\bar{\alpha}_1$  and  $\bar{\alpha}_2$ .

## B.2 | Linear Correlation Coefficient

Referring to Equations (B.1.1) and (B.1.6), if there is no correlation between  $x$  and  $y$ , then there are no trends for  $y$  to either increase or decrease with increasing  $x$ . Therefore, the least-squares fit must yield  $\bar{\alpha}_2 = 0$ . Now, consider the question of whether the data correspond to a straight line of the form:

$$x = \bar{\alpha}_1' + \bar{\alpha}_2' y \quad (\text{B.2.1})$$

The solution for  $\bar{\alpha}_2'$  is:

$$\bar{\alpha}_2' = \frac{N \sum x_i y_i - \sum x_i \sum y_i}{N \sum y_i^2 - (\sum y_i)^2} \quad (\text{B.2.2})$$

Again, if there is no correlation between  $x$  and  $y$ , then  $\bar{\alpha}_2' = 0$ . At the other extreme, if there is complete correlation between  $x$  and  $y$ , then there is a relationship between  $\bar{\alpha}_1$ ,  $\bar{\alpha}_2$ ,  $\bar{\alpha}_1'$ , and  $\bar{\alpha}_2'$  that is:

$$\begin{aligned} y &= -\frac{\bar{\alpha}_1'}{\bar{\alpha}_2'} + \frac{1}{\bar{\alpha}_2'} x = \bar{\alpha}_1 + \bar{\alpha}_2 x \\ \bar{\alpha}_1 &= -\frac{\bar{\alpha}_1'}{\bar{\alpha}_2'} \\ \bar{\alpha}_2 &= \frac{1}{\bar{\alpha}_2'} \end{aligned}$$

Thus, a perfect correlation gives  $\bar{\alpha}_2 \bar{\alpha}_2' = 1$  and no correlation yields  $\bar{\alpha}_2 \bar{\alpha}_2' = 0$  since both  $\bar{\alpha}_2$  and  $\bar{\alpha}_2'$  are zero for this condition. The linear correlation coefficient is therefore defined as:

$$\bar{R}_{cc} = \sqrt{\bar{\alpha}_2 \bar{\alpha}_2'} = \frac{N \sum x_i y_i - \sum x_i \sum y_i}{\left[ N \sum x_i^2 - (\sum x_i)^2 \right]^{1/2} \left[ N \sum y_i^2 - (\sum y_i)^2 \right]^{1/2}} \quad (\text{B.2.3})$$

The values of  $\bar{R}_{cc}$  are  $-1 \leq \bar{R}_{cc} \leq 1$  with  $\bar{R}_{cc} = 1$  and  $\bar{R}_{cc} = 0$  defining perfect and no correlations, respectively. Although the linear correlation coefficient is commonly quoted as a measure of “goodness of fit,” it is really not appropriate as a direct measure of the degree of correlation. If the data can be represented in a manner such that the fit should result in a y-intercept equal to zero, then a simple method can be used to determine the “goodness of fit.”

### B.3 | Correlation Probability with a Zero Y-Intercept

Numerous kinetic expressions can be placed into a form that would yield a zero y-intercept when using the linear least-squares method. A survey of a few of these models is provided in Table B.3.1. Given that the y-intercept is a known value (i.e., zero), if a perfect correlation could be achieved, the hypothesis that the true value of the parameter,  $\bar{\alpha}_1$ , is equal to the specified value,  $\bar{\alpha}_1^*$ , could be tested by referring the quantity:

$$\bar{t}^* = \frac{\bar{\alpha}_1 - \bar{\alpha}_1^*}{SE(\bar{\alpha}_1)} \quad (\text{B.3.1})$$

to the table of Student's  $\bar{t}^*$  values with  $N-2$  degrees of freedom. The standard error,  $SE$ , can be calculated as follows. The standard deviation  $\sigma_z$  of the determination of a parameter  $z$  is via the chain rule:

$$\sigma_z^2 = \sum \left[ \sigma_i^2 \left( \frac{\partial z}{\partial y_i} \right)^2 \right] \quad (\text{B.3.2})$$

where  $\sigma_i$  is the standard deviation of each datum point  $i$ . If  $\sigma_i = \sigma = \text{constant}$ , then  $\sigma_z^2$  is approximately equal to the sample variance, which is (P. R. Bevington, *Data*

**Table B.3.1** | Examples of kinetic relationships yielding zero intercepts.

Kinetics	Reactions	Relationship
1. 0th-order, irreversible (one-way), (constant volume)	$A \xrightarrow{k} \bar{P}$	$C_A^0 - C_A = kt$
2. First-order, irreversible (one-way)	$A \xrightarrow{k} \bar{P}$	$\ln\left[\frac{1}{1-f_A}\right] = kt$
3. First-order, reversible (two-way) <ul style="list-style-type: none"> <li>no product present at <math>t = 0</math></li> <li>product present at <math>t = 0</math>, <math>C_P^0</math></li> </ul>	$A \xrightleftharpoons[k_2]{k_1} \bar{P}$	$\ln\left[\frac{1}{1-(f_A/f_A^{\text{eq}})}\right] = \left(\frac{k_1}{f_A^{\text{eq}}}\right)t$ $\ln\left[\frac{1}{1-(f_A/f_A^{\text{eq}})}\right] = \left[\frac{k_1\left(\frac{C_P^0}{C_A^0} + 1\right)}{\left[\frac{C_P^0}{C_A^0} + f_A^{\text{eq}}\right]}\right]t$
4. Second-order, irreversible (one-way), (constant volume) <ul style="list-style-type: none"> <li><math>C_A^0 = C_B^0</math></li> <li><math>C_A^0 \neq C_B^0</math></li> </ul>	$A + B \xrightarrow{k} \bar{P}$	$\frac{1}{C_A} - \frac{1}{C_A^0} = kt$ $\ln\left[\frac{C_B C_A^0}{C_A C_B^0}\right] = (C_B^0 - C_A^0)kt$
5. Second-order, reversible (two-way) $C_A^0 = C_B^0$ , $C_C^0 = C_D^0 = 0$	$A + B \xrightleftharpoons[k_2]{k_1} C + D$	$\ln\left[\frac{f_A^{\text{eq}} - (2f_A^{\text{eq}} - 1)f_A}{(f_A^{\text{eq}} - f_A)}\right] = 2k_1\left[\frac{1}{f_A^{\text{eq}}} - 1\right]C_A^0 t$
6. Third-order, irreversible (one-way), (constant volume)	$A + 2B \xrightarrow{k} \bar{P}$ $A + B + C \xrightarrow{k} \bar{P}$	$\ln\left[\frac{C_B C_A^0}{C_A C_B^0}\right] - \frac{2\left[\frac{C_B^0}{C_A^0} - 2\right](C_A^0 - C_A)}{(C_B^0/C_A^0)C_B} = (C_A^0)^2\left[\frac{C_B^0}{C_A^0} - 2\right]kt$ $\ln\left(\frac{C_A^0}{C_A}\right) + \left[\frac{C_B^0/C_A^0 - 1}{\left(\frac{C_B^0}{C_A^0} - \frac{C_C^0}{C_A^0}\right)}\right]\ln\left(\frac{C_B^0}{C_B}\right) + \left[\frac{C_B^0/C_A^0 - 1}{\left(\frac{C_B^0}{C_A^0} - \frac{C_C^0}{C_A^0}\right)}\right]\ln\left(\frac{C_C^0}{C_C}\right) =$ $(C_A^0)^2\left[\frac{C_B^0}{C_A^0} - 1\right]\left[\frac{C_C^0}{C_A^0} - 1\right]kt$
7. $n$ th-order, irreversible (one-way), (constant volume)	$A \xrightarrow{k} \bar{P}$	$(C_A)^{(1-n)} - (C_A^0)^{(1-n)} = (n-1)kt$



*Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill, New York, 1969, p. 114):

$$\sigma^2 \cong \frac{1}{N-2} \sum (y_i - \bar{\alpha}_1 - \bar{\alpha}_2 x_i)^2 \quad (\text{B.3.3})$$

for the linear equation (B.1.1). (The sample variance is the sum of squares of the residuals divided by the number of data points minus the number of parameters fitted.) Now Equation (B.3.2) written for the linear equation (B.1.1) gives:

$$\left. \begin{aligned} \sigma_{\bar{\alpha}_1}^2 &= \sigma^2 \sum \left( \frac{\partial \bar{\alpha}_1}{\partial y_i} \right)^2 \\ \sigma_{\bar{\alpha}_2}^2 &= \sigma^2 \sum \left( \frac{\partial \bar{\alpha}_2}{\partial y_i} \right)^2 \end{aligned} \right\} \quad (\text{B.3.4})$$

Using Equation (B.1.6) to calculate the partial derivatives in Equation (B.3.4) yields:

$$\sigma_{\bar{\alpha}_1}^2 = \frac{\sigma^2}{\Delta} (\sum x_i^2) \quad (\text{B.3.5})$$

$$\sigma_{\bar{\alpha}_2}^2 = \frac{N\sigma^2}{\Delta} \quad (\text{B.3.6})$$

where

$$\Delta = N \sum x_i^2 - (\sum x_i)^2$$

Thus,  $SE(\bar{\alpha}_1) = \sigma_{\bar{\alpha}_1}$  and  $SE(\bar{\alpha}_2) = \sigma_{\bar{\alpha}_2}$ . Now returning to Equation (B.3.1),  $\bar{t}^*$  is the experimental deviation over the standard error and if this value is larger than the value in a Student's  $\bar{t}^*$ -distribution table (see any text on statistics for this table) for a given degree of confidence, for example, 95 percent ( $\bar{t}_{\text{exp}}^*$  = expected deviation/standard error), then the hypothesis is rejected, that is, the  $y$ -intercept is significantly different than zero. If  $\bar{t}^* < \bar{t}_{\text{exp}}^*$  then the hypothesis is accepted and  $\bar{\alpha}_2$  can be reported as:

$$\bar{\alpha}_2 \pm \sigma_{\bar{\alpha}_2} \quad (\text{B.3.7})$$

## B.4 | Nonlinear Regression

There are numerous methods for performing nonlinear regression. Here, a simple analysis is presented in order to provide the reader the general concepts used in performing a nonlinear regression analysis.

To begin a nonlinear regression analysis, the model function must be known. Let:

$$y = f(x, \mathbf{a}) \quad (\text{B.4.1})$$

where the function  $f$  is nonlinear in the dependent variable  $x$  and unknown parameters designated by the set  $\mathbf{a} = [a_1, a_2, \dots, a_n]$ . A least-squares fit of the observed

measurements  $y_i$  to the function shown in Equation (B.4.1) can be performed as follows. First, define  $\bar{X}^2$  [for linear regression see Equation (B.1.5)] as:

$$\bar{X}^2 = \sum_{i=1}^N \left[ \frac{y_i - y(x_i)}{\sigma_i} \right] = \sum_{i=1}^N \left\{ \frac{1}{\sigma^2} [y_i - f(x_i, \mathbf{a})]^2 \right\} \quad (\text{B.4.2})$$

As with linear least squares analysis,  $\bar{X}^2$  is minimized as follows. The partial derivatives of  $\bar{X}^2$  with respect to the parameters of  $\mathbf{a}$  are set equal to zero, for example, with  $a_1$ :

$$0 = \frac{\partial \bar{X}^2}{\partial a_1} = \frac{\partial}{\partial a_1} \left\{ \frac{1}{\sigma^2} \sum_{i=1}^N [y_i - f(x_i, \mathbf{a})]^2 \right\} = \frac{-2}{\sigma^2} \sum_{i=1}^N [y_i - f(x_i, \mathbf{a})] \frac{\partial f(x_i, \mathbf{a})}{\partial a_1} \quad (\text{B.4.3})$$

Thus, there will be  $n$  equations containing the  $n$  parameters of  $\mathbf{a}$ . These equations involve the function  $f(x_i, \mathbf{a})$  and the partial derivatives of the function, that is,

$$\frac{\partial f(x_i, \mathbf{a})}{\partial a_j}, \quad \text{for } j = 1, \dots, n$$

The set of  $n$  equations of the type shown in Equation (B.4.3) needs to be solved. This set of equations is nonlinear if  $f(x_i, \mathbf{a})$  is nonlinear. Thus, the solution of this set of equations requires a nonlinear algebraic equation solver. These are readily available. For information on the type of solution, consult any text on numerical analysis. Since the solution involves a set nonlinear algebraic equation, it is performed by an iterative process. That is, initial guesses for the parameters  $\mathbf{a}$  are required. Often, the solution will terminate at local minimum rather than the global minimum. Thus, numerous initial guesses should be used to assure that the final solution is independent of the initial guess.

The issue of “goodness-of-fit” with nonlinear regression is not straightforward. Numerous methods can be used to explore the “goodness-of-fit” of the model to the data (e.g., residual analysis, variance analysis, and Chi-squared analysis). It is always a good idea to inspect the plot of the predicted  $[y(x_i)]$  versus observed  $y_i$  values to watch for systematic deviations. Additionally, some analytical measure for “goodness-of-fit” should also be employed.

## Transport in Porous Media

### C.1 | Derivation of Flux Relationships in One-Dimension

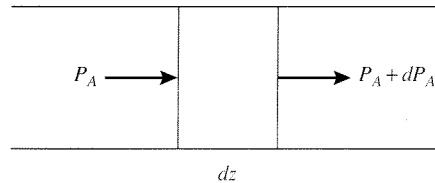
Consider a tube filled with an isobaric binary gas mixture of components  $A$  and  $B$ . When component  $A$  moves it exerts a force on  $B$ . This frictional force,  $\overline{f}_{AB}$ , can be described as:

$$\overline{f}_{AB} = (\text{proportionality constant}) \underbrace{(\text{concentration of } A)(\text{concentration of } B)}_{\text{number of collisions}} \underbrace{(\text{relative velocity of } A \text{ to } B)}_{\text{momentum exchange per collision}}$$

or

$$\overline{f}_{AB} = (\text{const})_{AB} C_A C_B (V_A - V_B) \quad (\text{C.1.1})$$

where  $V_i$  is the molecular velocity of species  $i$ . The total frictional losses have to equal the driving force. Thus, for the section  $dz$ ,



$$\frac{-dP_A}{dz} = (\text{const})_{AB} C_A C_B (V_A - V_B) \quad (\text{C.1.2})$$

Multiply Equation (C.1.2) by  $C$  (total concentration) and rearrange to give:

$$-CP \frac{dX_A}{dz} = (\text{const})_{AB} CC_A C_B (V_A - V_B)$$

$$\begin{aligned}\frac{-CP}{(\text{const})_{AB} C_A C_B} \frac{dX_A}{dz} &= C(V_A - V_B) \\ \frac{-R_s T}{(\text{const})_{AB} X_A X_B} \frac{dX_A}{dz} &= C(V_A - V_B)\end{aligned}\quad (\text{C.1.3})$$

If the proportionality factor is defined as:

$$(\text{const})_{AB} = \frac{R_s T}{CD_{AB}} \quad (\text{C.1.4})$$

then Equation (C.1.3) can be written as follows:

$$\frac{-CD_{AB}}{X_A X_B} \frac{dX_A}{dz} = C(V_A - V_B) \quad (\text{C.1.5})$$

Equation (C.1.5) is Fick's First Law. To see this, rearrange Equation (C.1.5) as shown below:

$$\begin{aligned}C X_A X_B (V_A - V_B) &= -CD_{AB} \frac{dX_A}{dz} \\ C_A (X_B V_A - X_B V_B) &= -CD_{AB} \frac{dX_A}{dz}\end{aligned}\quad (\text{C.1.6})$$

Recall that Fick's First Law is:

$$\bar{J}_A = -CD_{AB} \frac{dX_A}{dz} = C_A (V_A - V_{\text{total}}) \quad (\text{C.1.7})$$

where  $\bar{J}_A$  is the flux of  $A$  with respect to a coordinate system that is moving at  $V_{\text{total}}$  and:

$$V_{\text{total}} = X_A V_A + X_B V_B$$

Further arrangements of Equation (C.1.6) can be made as shown below:

$$\begin{aligned}C_A (X_B V_A - X_B V_B + X_A V_A - X_A V_A) &= -CD_{AB} \frac{dX_A}{dz} \\ C_A (-X_A V_A - X_B V_B + X_A V_A + X_B V_A) &= -CD_{AB} \frac{dX_A}{dz} \\ C_A (V_A - V_{\text{total}}) &= -CD_{AB} \frac{dX_A}{dz}\end{aligned}$$

which is Equation (C.1.7).

Now consider a multicomponent system. For a multicomponent mixture of  $NCOMP$  species:

$$ff_{ij} = \frac{R_g T C_i C_j}{CD_{ij}} (V_i - V_j) \quad (C.1.8)$$

by analogy to the frictional force for a binary mixture [Equation (C.1.1) with Equation (C.1.4)]. Using Equation (C.1.8) gives a total force balance of:

$$\frac{-dX_i}{dz} = \sum_{\substack{j=1 \\ i \neq j}}^{NCOMP} \frac{X_i X_j (V_i - V_j)}{D_{ij}} \quad (C.1.9)$$

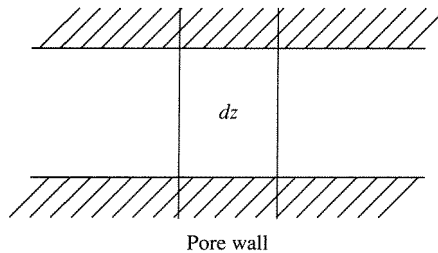
that is the Stefan-Maxwell equations.

The Stefan-Maxwell equations are normally written in terms of fluxes,  $N_i$ . Since  $N_i = C_i V_i$ , Equation (C.1.9) can be expressed in terms of fluxes as:

$$\frac{-dX_i}{dz} = \sum_{\substack{j=1 \\ i \neq j}}^{NCOMP} \left[ \frac{X_j N_i - X_i N_j}{CD_{ij}} \right] \quad (C.1.10)$$

## C.2 | Flux Relationships in Porous Media

Consider the movement of a binary gas mixture in a pore:



The loss of momentum in  $dz$  due to molecule-wall collisions is:

$$(dP_A)_K (g_c A_C^P) = N_A \frac{R_g T}{D_{KA}} dz (g_c A_C^P) \quad (C.2.1)$$

where

$g_c$  = gravitational constant

$A_C^P$  = cross-sectional area of the pore

$D_{KA}$  = Knudsen diffusion coefficient of A

$(dP_A)_K$  = change in pressure from molecule-wall collisions

Fick's First Law is (momentum losses due to molecule-molecule collisions):

$$N_A = \bar{J}_A + X_A(N_A + N_B) = -\frac{D_{AB}}{R_g T} \frac{dX_A}{dz} + X_A(N_A + N_B) \quad (\text{C.2.2})$$

(diffusive flux) + (bulk flow)

Let:

$$FR = 1 + N_B/N_A \quad (\text{C.2.3})$$

so that Equation (C.2.2) can be written as:

$$N_A = \frac{-D_{AB}}{[1 - (FR)X_A]R_g T} \frac{dX_A}{dz} \quad (\text{C.2.3})$$

or

$$-(dP_A)_{mm} g_c A_C^P = N_A \frac{R_g T}{D_{AB}} [1 - (FR)X_A] dz (g_c A_C^P) \quad (\text{C.2.4})$$

where  $(dP_A)_{mm}$  is the change in pressure from molecule-molecule collisions. Now the total momentum loss due to molecule-wall and molecule-molecule collisions is the sum of Equation (C.2.1) and Equation (C.2.4)  $[(dP_A) = (dP_A)_K + (dP_A)_{mm}]$ :

$$-(dP_A) g_c A_C^P = N_A \frac{R_g T}{D_{KA}} dz g_c A_C^P + N_A \frac{R_g T}{D_{AB}} [1 - (FR)X_A] dz (g_c A_C^P)$$

or after rearrangement:

$$N_A = \frac{-1}{\left[ \frac{1 - (FR)X_A}{D_{AB}} + \frac{1}{D_{KA}} \right]} \frac{1}{R_g T} \frac{dP_A}{dz} \quad (\text{C.2.5})$$

If there is equimolar counterdiffusion ( $N_A = -N_B$ ) and/or if  $X_A$  is small, Equation (C.2.5) reduces to:

$$N_A = \frac{-1}{\frac{1}{D_{AB}} + \frac{1}{D_{KA}}} \frac{1}{R_g T} \frac{dP_A}{dz} = \frac{-D_{TA}}{R_g T} \frac{dP_A}{dz} \quad (\text{C.2.6})$$

where

$$\frac{1}{D_{TA}} = \frac{1}{D_{AB}} + \frac{1}{D_{KA}} \quad (\text{C.2.7})$$

Equation (C.2.7) is called the Bosanquet equation.

A momentum balance for multicomponent mixtures can be formulated in a manner analogous to that used to derive Equation (C.2.4) using molecule-wall and molecule-molecule (Stefan-Maxwell) relationships to give:

$$-(dP_i)_{g_c} A_C^p = \frac{N_i R_g T}{D_{Ki}} dz g_c A_C^p + \sum_{\substack{j=1 \\ i \neq j}}^{NCOMP} \frac{R_g T}{D_{ij}} (X_j N_i - X_i N_j) dz g_c A_C^p$$

or

$$\frac{-1}{R_g T} \frac{dP_i}{dz} = \sum_{\substack{j=1 \\ i \neq j}}^{NCOMP} \left[ \frac{X_j N_i - X_i N_j}{D_{ij}} \right] + \frac{N_i}{D_{Ki}} \quad (\text{C.2.8})$$





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