

❖ Rate Law for Opposing Reactions of 1st Order and 2nd Order

A reaction will be called as the opposing or reversible reaction if the reactants react together to form a product and the products also react to yield the reactants simultaneously under the same conditions.

In a simple context, we can say these reactions proceed not only in the forward direction but also in the backward direction. These reactions can be classified into the following categories based upon the kinetic order of the reactions involved.

➤ First Order Opposed by First Order

In order to understand the kinetic profile of first-order reactions opposed by the first order, consider a general reaction in which the reactant A forms product B i.e.



Now, if $k_f \gg k_b$, k_b can be neglected. However, k_f and k_b have comparable values, a rate law depending upon both the constants can be written. To do so, suppose that a is the initial concentration of the reactant A and x is the decrease in the concentration of A after 't' time. The concentration of the product after the same time would also be equal to x . Hence, the rates of forward reaction (R_f) and backward reaction (R_b) can be given as:

$$R_f = k_f[A] = k_f(a - x) \quad (17)$$

$$R_b = k_b[B] = k_b x \quad (18)$$

The net reaction rate i.e. rate of formation of the product can be given as

$$\frac{dx}{dt} = k_f(a - x) - k_b x \quad (19)$$

However, when the equilibrium is attained, the rate of forward reaction will be equal to the rate of backward reaction i.e. $R_f = R_b$. Therefore, the will take the form

$$k_f(a - x_{eq}) = k_b x_{eq} \quad (20)$$

Where x_{eq} is the concentration of product B or the decrease in the concentration of reactant A at equilibrium. Now putting the value of k_b from equation (20) into equation (19), we get

$$\frac{dx}{dt} = k_f(a - x) - \frac{k_f(a - x_{eq})}{x_{eq}} x \quad (21)$$

$$\frac{dx}{dt} = k_f \left[(a - x) - \frac{(a - x_{eq})}{x_{eq}} x \right] \quad (22)$$

or

$$\frac{dx}{dt} = k_f \left[\frac{(a-x)x_{eq} - (a-x_{eq})x}{x_{eq}} \right] \quad (23)$$

$$\frac{dx}{dt} = k_f \frac{ax_{eq} - ax}{x_{eq}} = \frac{k_f a(x_{eq} - x)}{x_{eq}} \quad (24)$$

or

$$\frac{x_{eq}}{(x_{eq} - x)} dx = k_f a dt \quad (25)$$

Integrating equation (25), we get

$$-x_{eq} \ln(x_{eq} - x) = k_f a t + C \quad (26)$$

Where C is the constant of integration. When $t = 0$, $x = 0$; putting these values in equation (26), we get

$$-x_{eq} \ln x_{eq} = C \quad (27)$$

Using the value of C from equation (27) in (26)

$$-x_{eq} \ln(x_{eq} - x) = k_f a t - x_{eq} \ln x_{eq} \quad (28)$$

or

$$x_{eq} \ln x_{eq} - x_{eq} \ln(x_{eq} - x) = k_f a t \quad (29)$$

$$k_f = \frac{x_{eq}}{at} \ln \frac{x_{eq}}{x_{eq} - x} \quad (30)$$

Using equation (30), the rate constant for the forward reaction can easily be determined by measuring simple quantities like a , t , x_{eq} and x . Now rearranging equation (20) for k_b

$$k_b = \frac{k_f(a - x_{eq})}{x_{eq}} \quad (31)$$

$$k_b = \frac{k_f(a - x_{eq})}{x_{eq}} = k_f \left(\frac{a}{x_{eq}} - \frac{x_{eq}}{x_{eq}} \right) = k_f \left(\frac{a}{x_{eq}} - 1 \right) \quad (32)$$

Now putting the value k_f from equation (30) in equation (32), we get

$$k_b = \left(\frac{1}{t} \ln \frac{x_{eq}}{x_{eq} - x} \right) - \frac{x_{eq}}{at} \ln \frac{x_{eq}}{x_{eq} - x} \quad (33)$$

Hence, the value of the rate constant for backward reaction can also be obtained just by measuring t , x_{eq} and x ; or in other words, the k_f eventually yields the k_b also.

Alternatively, the values of k_f and k_b can also be obtained a slightly different route. Rearranging equation (30), we get

$$\frac{a k_f}{x_{eq}} = \frac{1}{t} \ln \frac{x_{eq}}{x_{eq} - x} \quad (34)$$

Also rearranging equation (20), we have

$$\frac{k_f a}{x_{eq}} = k_b + k_f \quad (35)$$

Equating the right-hand sides of equation (34) and (35), we get

$$\frac{1}{t} \ln \frac{x_{eq}}{x_{eq} - x} = k_b + k_f \quad (36)$$

$$\ln \frac{x_{eq}}{x_{eq} - x} = (k_b + k_f)t \quad (37)$$

or

$$\log \frac{x_{eq}}{x_{eq} - x} = \frac{(k_b + k_f)}{2.303} t \quad (38)$$

Equation (37) and (38) are the equations of straight line ($y = mx + c$) with zero intercept.

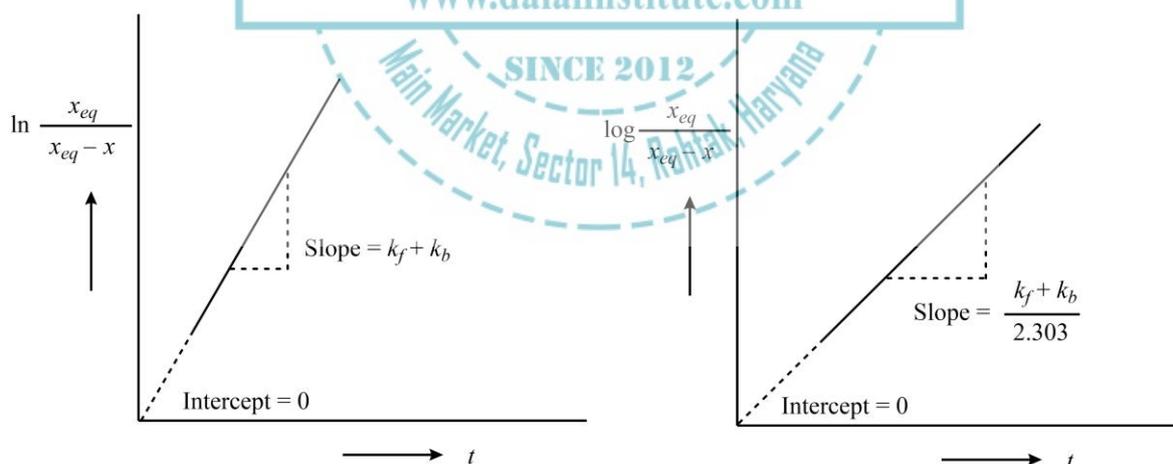


Figure 6. The plot of $\ln \frac{x_{eq}}{x_{eq} - x}$ and $\log \frac{x_{eq}}{x_{eq} - x}$ vs time for first order opposed by the first order.

Now, finding $k_f + k_b$ from slope and k_f/k_b from equilibrium constant, k_f and k_b can easily be obtained from the elimination method. It should also be noted that if plot $\ln \frac{x_{eq} - x}{x_{eq}}$ and $\log \frac{x_{eq} - x}{x_{eq}}$, the slopes will become negative.

➤ **First Order Opposed by Second Order**

In order to understand the kinetic profile of first-order reactions opposed by second-order, consider a general reaction in which the reactant A forms product B and C i.e.



Now, if $k_f \gg k_b$, k_b can be neglected. However, k_f and k_b have comparable values, a rate law depending upon both the constants can be written. To do so, suppose that a is the initial concentration of the reactant A and x is the decrease in the concentration of A after 't' time. The concentration of both the products after same time would also be equal to x . Hence, the rates of forward reaction (R_f) and backward reaction (R_b) can be given as:

$$R_f = k_f[A] = k_f(a - x) \quad (40)$$

$$R_b = k_b[B][C] = k_b x^2 \quad (41)$$

The net reaction rate i.e. rate of formation of the product can be given as

$$\frac{dx}{dt} = k_f(a - x) - k_b x^2 \quad (42)$$

However, when the equilibrium is attained, the rate of forward reaction will be equal to the rate of backward reaction i.e. $R_f = R_b$. Therefore, the equation (42) will take the form

$$k_f(a - x_{eq}) = k_b x_{eq}^2 \quad (43)$$

Where x_{eq} is the concentration of product B and C or the decrease in the concentration of reactant A at equilibrium. Now putting the value of k_b from equation (43) into equation (42), we get

$$\frac{dx}{dt} = k_f(a - x) - \frac{k_f(a - x_{eq})}{x_{eq}^2} x^2 \quad (44)$$

$$\frac{dx}{dt} = k_f \left[(a - x) - \frac{(a - x_{eq})}{x_{eq}^2} x^2 \right] \quad (45)$$

or

$$\frac{dx}{dt} = k_f \left[\frac{(a - x)x_{eq}^2 - (a - x_{eq})x^2}{x_{eq}^2} \right] \quad (46)$$

$$\frac{dx}{dt} = k_f \left[\frac{ax_{eq}^2 - xx_{eq}^2 - ax^2 + x_{eq}x^2}{x_{eq}^2} \right] \quad (47)$$

or

$$\frac{x_{eq}^2}{(ax_{eq}^2 - xx_{eq}^2 - ax^2 + x_{eq}x^2)} dx = k_f dt \quad (48)$$

Integrating equation (48), and then rearranging

$$k_f = \frac{x_{eq}}{t(2a - x_{eq})} \ln \frac{ax_{eq} + x_{eq}(a - x_{eq})}{a(x_{eq} - x)} \quad (49)$$

Using equation (49), the rate constant for the forward reaction can easily be determined by measuring simple quantities like a , t , x_{eq} and x . Now, we know that the equilibrium constant for the first order opposed by second-order will be

$$K = \frac{[B][C]}{[A]} \quad (50)$$

also

$$K = \frac{k_f}{k_b} \quad (51)$$

Now putting the value of k_f from equation (49) in equation (51) and the rearranging for k_b , we get

$$k_b = \frac{x_{eq}}{t(2a - x_{eq})K} \ln \frac{ax_{eq} + x_{eq}(a - x_{eq})}{a(x_{eq} - x)} \quad (52)$$

Hence, the value of the rate constant for backward reaction can also be obtained just by measuring t , x_{eq} and x and the equilibrium constant from equation (50).

➤ Second Order Opposed by First Order

In order to understand the kinetic profile of second-order reactions opposed by first order, consider a general reaction in which two reactants A and B form product C i.e.



Now, if $k_f \gg k_b$, k_b can be neglected. However, k_f and k_b have comparable values, a rate law depending upon both the constants can be written. To do so, suppose that a is the initial concentration of both the reactant A and B ; while x is the decrease in the concentrations of both reactants after 't' time. The concentration of the product after the same time would also be equal to x . Hence, the rates of forward reaction (R_f) and backward reaction (R_b) can be given as:

$$R_f = k_f[A][B] = k_f(a - x)^2 \quad (54)$$

$$R_b = k_b[C] = k_b x \quad (55)$$

The net reaction rate i.e. rate of formation of the product can be given as

$$\frac{dx}{dt} = k_f(a-x)^2 - k_b x \quad (56)$$

However, when the equilibrium is attained, the rate of forward reaction will be equal to the rate of backward reaction i.e. $R_f = R_b$. Therefore, the equation (56) will take the form

$$k_f(a-x_{eq})^2 = k_b x_{eq} \quad (57)$$

Where x_{eq} is the concentration of the product C or the decrease in the concentration of reactant A or B at equilibrium. Now putting the value of k_b from equation (57) into equation (56), we get

$$\frac{dx}{dt} = k_f(a-x)^2 - \frac{k_f(a-x_{eq})^2}{x_{eq}} x \quad (58)$$

$$\frac{dx}{dt} = k_f \left[(a-x)^2 - \frac{(a-x_{eq})^2}{x_{eq}} x \right] \quad (59)$$

or

$$\frac{dx}{dt} = k_f \left[\frac{(a-x)^2 x_{eq} - (a-x_{eq})^2 x}{x_{eq}} \right] \quad (60)$$

$$\frac{dx}{dt} = k_f \left[\frac{(a^2 + x^2 - 2ax)x_{eq} - (a^2 + x_{eq}^2 - 2ax_{eq})x}{x_{eq}} \right] \quad (61)$$

$$\frac{dx}{dt} = k_f \left[\frac{a^2 x_{eq} + x^2 x_{eq} - 2ax x_{eq} - a^2 x - x_{eq}^2 x + 2ax_{eq} x}{x_{eq}} \right] \quad (62)$$

$$\frac{dx}{dt} = k_f \left[\frac{a^2 x_{eq} + x^2 x_{eq} - a^2 x - x_{eq}^2 x}{x_{eq}} \right] \quad (63)$$

or

$$\frac{x_{eq}}{(a^2 x_{eq} + x^2 x_{eq} - a^2 x - x_{eq}^2 x)} dx = k_f dt \quad (64)$$

Integrating equation (64), and then rearranging

$$k_f = \frac{x_{eq}}{t(a^2 - x_{eq}^2)} \ln \frac{x_{eq}(a^2 - x_{eq}x)}{a^2(x_{eq} - x)} \quad (65)$$

Using equation (66), the rate constant for the forward reaction can easily be determined by measuring simple quantities like a , t , x_{eq} and x . Now, we know that the equilibrium constant for a second-order reaction opposed by first order will be

$$K = \frac{[C]}{[A][B]} \quad (66)$$

$$K = \frac{k_f}{k_b} \quad (67)$$

Now putting the value of k_f from equation (65) in equation (67) and the rearranging for k_b , we get

$$k_b = \frac{x_{eq}}{t(a^2 - x_{eq}^2)K} \ln \frac{x_{eq}(a^2 - x_{eq}x)}{a^2(x_{eq} - x)} \quad (68)$$

Hence, the value of the rate constant for backward reaction can also be obtained just by measuring t , x_{eq} and x and the equilibrium constant from equation (66).

➤ **Second Order Opposed by Second Order**

In order to understand the kinetic profile of second-order reactions opposed by second-order, consider a general reaction in which two reactants A and B form product C and D i.e.



Now, if $k_f \gg k_b$, k_b can be neglected. However, k_f and k_b have comparable values, a rate law depending upon both the constants can be written. To do so, suppose that a is the initial concentration of both the reactant A and B ; while x is the decrease in the concentrations of both reactants after 't' time. The concentration of the products after the same time would also be equal to x . Hence, the rates of forward reaction (R_f) and backward reaction (R_b) can be given as:

$$R_f = k_f[A][B] = k_f(a - x)^2 \quad (70)$$

$$R_b = k_b[C][D] = k_b x^2 \quad (71)$$

The net reaction rate i.e. rate of formation of the product can be given as

$$\frac{dx}{dt} = k_f(a - x)^2 - k_b x^2 \quad (72)$$

However, when the equilibrium is attained, the rate of forward reaction will be equal to the rate of backward reaction i.e. $R_f = R_b$. Therefore, the equation (72) will take the form

$$k_f(a - x_{eq})^2 = k_b x_{eq}^2 \quad (73)$$

Where x_{eq} is the concentration of the product C and D or the decrease in the concentration of reactant A or B at equilibrium. Now putting the value of k_b from equation (73) into equation (72), we get

$$\frac{dx}{dt} = k_f(a-x)^2 - \frac{k_f(a-x_{eq})^2}{x_{eq}^2}x^2 \quad (74)$$

$$\frac{dx}{dt} = k_f \left[(a-x)^2 - \frac{(a-x_{eq})^2}{x_{eq}^2}x^2 \right] \quad (75)$$

or

$$\frac{dx}{dt} = k_f \left[\frac{(a-x)^2x_{eq}^2 - (a-x_{eq})^2x^2}{x_{eq}^2} \right] \quad (76)$$

$$\frac{dx}{dt} = k_f \left[\frac{a^2x_{eq}^2 + x^2x_{eq}^2 - 2axx_{eq}^2 - a^2x^2 - x_{eq}^2x^2 + 2ax_{eq}x^2}{x_{eq}^2} \right] \quad (78)$$

or

$$\frac{x_{eq}^2}{(a^2x_{eq}^2 - 2axx_{eq}^2 - a^2x^2 + 2ax_{eq}x^2)} dx = k_f dt \quad (80)$$

Integrating equation (80), and then rearranging

$$k_f = \frac{x_{eq}}{2at(a-x_{eq})} \ln \frac{x(a-2x_{eq}) + ax_{eq}}{a(x_{eq}-x)} \quad (81)$$

Using equation (81), the rate constant for the forward reaction can easily be determined by measuring simple quantities like a , t , x_{eq} and x . Now, we know that the equilibrium constant for a second-order reaction opposed by second-order will be

$$K = \frac{[C][D]}{[A][B]} \quad (82)$$

$$K = \frac{k_f}{k_b} \quad (83)$$

Now putting the value of k_f from equation (81) in equation (83) and the rearranging for k_b , we get

$$k_b = \frac{x_{eq}}{2at(a-x_{eq})K} \ln \frac{x(a-2x_{eq}) + ax_{eq}}{a(x_{eq}-x)} \quad (84)$$

Hence, the value of the rate constant for backward reaction can also be obtained just by measuring t , x_{eq} and x and the equilibrium constant from equation (84).

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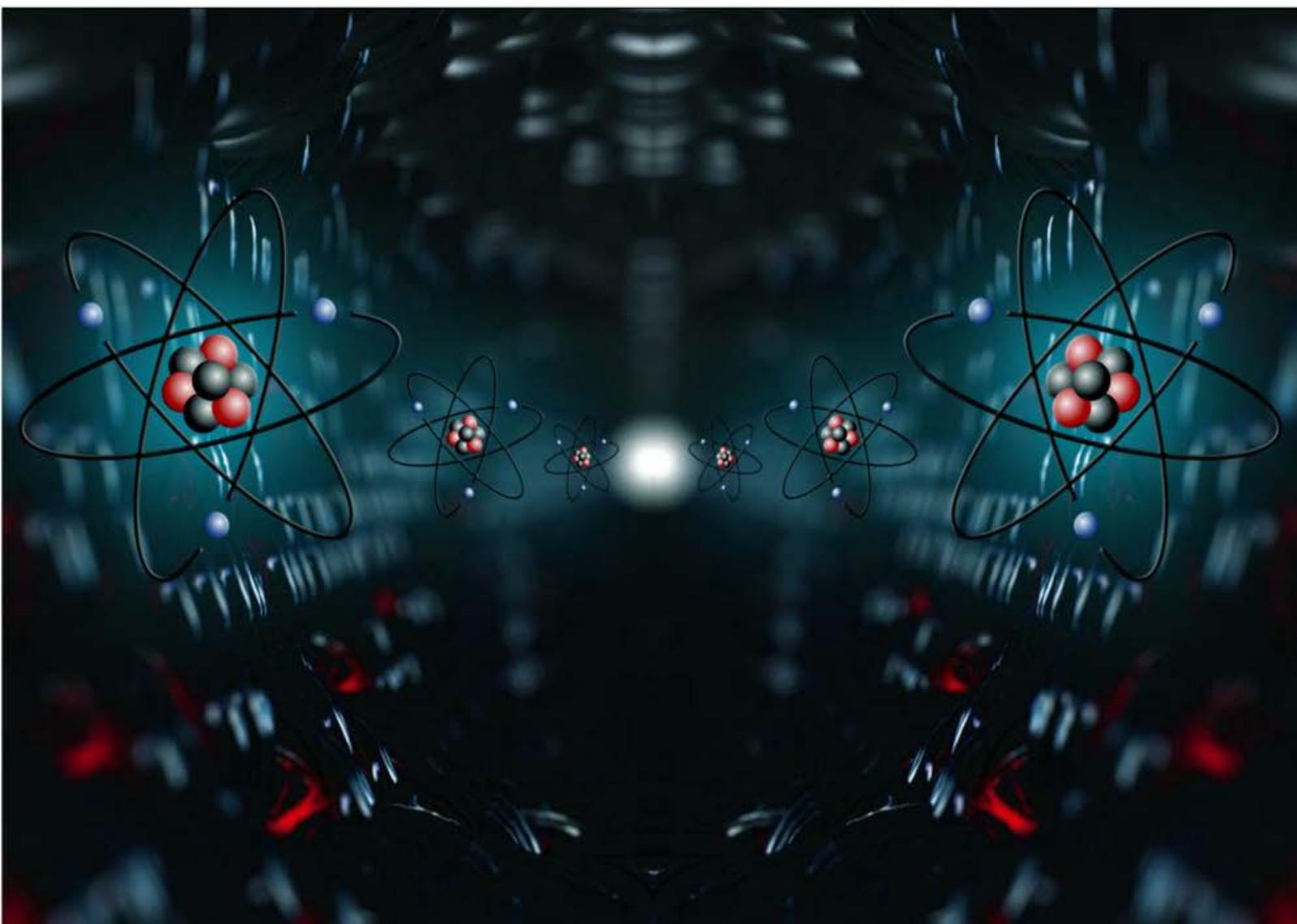
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Volume I

MANDEEP DALAL



First Edition

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