
B. General Rate and Equilibrium Equations

B.1 General rate equations

The rate of a reaction can be defined as the change in the concentration of a reactant or product over time. Consider the following reaction:



The reaction rate for the above-mentioned reaction is given by:

$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = k_1[A]^m[B]^n - k_{-1}[C] \quad \text{B.2}$$

The constant k_1 as a proportional constant (the forward rate constant), that relates the rate of change to the reagent concentrations ([] denotes concentration) and the minus signs indicate the disappearance of A and B. The values m and n represent the order of the reaction with regard to the concentrations of A and B, with the sum of m and n equal to the order of the rate law (total reaction). The order is the way in which the rate varies with a change in concentration of one or both of the reacting species. These values can be determined experimentally, but this is often difficult. This problem is circumvented by using pseudo-first order conditions, where $[B] \gg [A]$ and $[C]$.

The expression for the observed pseudo-first order rate constant (after integration), is:

$$k_{\text{obs}} = k_1[B]^n + k_{-1} \quad \text{B.3}$$

Pseudo-first order conditions (with $[B]$ at least 10 times in excess of $[A]$) resulting in eq. B.3, also serve to obtain the rate constant by determining k_{obs} at different

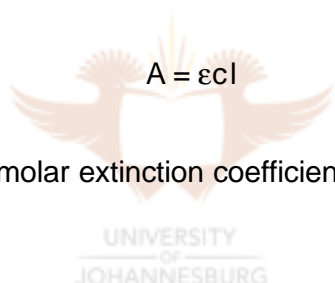
concentrations of B. It can furthermore be used to simplify second order reactions. If the value of $m = 1$, then the reaction is first order in B and a graph of k_{obs} against $[B]$ will be a straight line with an intercept of k_1 to indicate that there is an equilibrium (reverse reaction) or parallel reaction. In the case of an equilibrium reaction, the equilibrium constant is given by eq. B.4,

$$K_{\text{eq}} = \frac{k_1}{k_{-1}} \quad \text{B.4}$$

By integrating eq. B.2 between time = 0 and t respectively the following equation (expressed in terms of C) is obtained:

$$\ln \frac{[C]_t}{[C]_0} = k_{\text{obs}} t \quad \text{B.5}$$

The Beer's law states that:

$$A = \epsilon c l \quad \text{B.6}$$


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with A the absorbance, ϵ the molar extinction coefficient, c the concentration and l the light path length.

If the Beer' law is incorporated into eq. B.4 (with $\frac{[C]_t}{[C]_0} = \frac{A_\infty - A_t}{A_\infty - A_0}$) and manipulated, the following equation results:

$$A_t = A_\infty - (A_\infty - A_0)e^{-k_{\text{obs}} t} \quad \text{B.7}$$

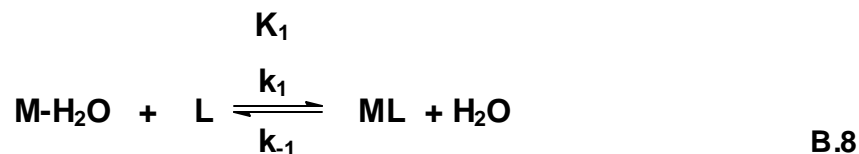
A_t and A_∞ is the absorbance after time t and infinite time respectively. The term "infinite time" is defined as the time at which the reaction is complete for all practical purposes. The observed rate constant, k_{obs} , can be obtained from a least-squares fit of the absorbance vs. time data for a first order reaction using eq. B.7.

All the absorbance vs. time data for the kinetic reactions in this study was fitted to eq. B.7.

B.2 Derivation of the equation for the equilibrium constant

For the spectrophotometric determination of K_1 .

For the following reaction between a metal complex and a monodentate ligand:



$$K_1 = \frac{[\text{ML}]}{[\text{MH}_2\text{O}][\text{L}]} \quad \text{B.9}$$

$$[\text{MH}_2\text{O}] = \frac{[\text{ML}]}{K_1[\text{L}]} \quad \text{B.10}$$

$$[\text{ML}] = K_1[\text{MH}_2\text{O}][\text{L}] \quad \text{B.11}$$

$$[\text{M}]_{\text{tot}} = [\text{MH}_2\text{O}] + [\text{ML}] \quad \text{B.12}$$

Substituting eq. B.11 into eq. B.12 gives:

$$[\text{M}]_{\text{tot}} = [\text{MH}_2\text{O}] + K_1[\text{MH}_2\text{O}][\text{L}] \quad \text{B.13}$$

$$[\text{M}]_{\text{tot}} = [\text{MH}_2\text{O}] (1 + K_1[\text{L}]) \quad \text{B.14}$$

$$[\text{MH}_2\text{O}] = [\text{M}]_{\text{tot}} / (1 + K_1[\text{L}]) \quad \text{B.15}$$

Substituting eq. B.15 into eq. B.12 gives:

$$[\text{M}]_{\text{tot}} = [\text{ML}] / K_1[\text{L}] + [\text{ML}] \quad \text{B.16}$$

$$[\text{M}]_{\text{tot}} = [\text{ML}] (1/K_1[\text{L}] + 1) \quad \text{B.17}$$

$$[\text{ML}] = \frac{[\text{M}]_{\text{tot}}}{\frac{1}{K_1[\text{L}]} + 1} \times \frac{K_1[\text{L}]}{K_1[\text{L}]} \quad \text{B.18}$$

$$[\text{ML}] = \frac{[\text{M}]_{\text{tot}} K_1[\text{L}]}{1 + K_1[\text{L}]} \quad \text{B.19}$$

$$A_{\text{obs}} = e_{\text{MH}_2\text{O}} A_{\text{MH}_2\text{O}} + e_{\text{ML}} A_{\text{ML}} \quad \text{B.20}$$

$$A_{\text{obs}} = e_{\text{MH}_2\text{O}} \left(\frac{[\text{M}]_{\text{tot}}}{1 + K_1[\text{L}]} \right) + e_{\text{ML}} \left(\frac{[\text{M}]_{\text{tot}} K_1[\text{L}]}{1 + K_1[\text{L}]} \right) \quad \text{B.21}$$

With $A_{\text{MH}_2\text{O}} = \varepsilon_{\text{MH}_2\text{O}}[\text{M}]_{\text{tot}}$ and $A_{\text{ML}} = \varepsilon_{\text{ML}}[\text{M}]_{\text{tot}}$

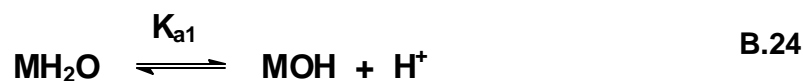
$$A_{\text{obs}} = \left(\frac{[\text{M}]_{\text{MH}_2\text{O}}}{1 + K_1[\text{L}]} \right) + \left(\frac{[\text{M}]_{\text{ML}} K_1[\text{L}]}{1 + K_1[\text{L}]} \right) \quad \text{B.22}$$

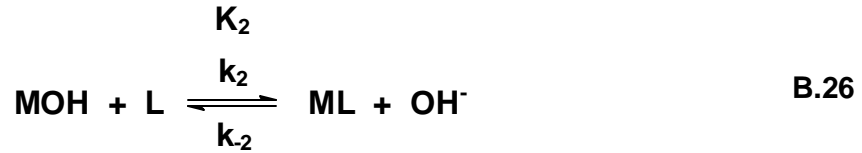
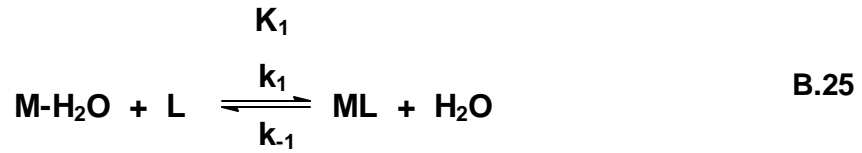
$$A_{\text{obs}} = \frac{A_{\text{MH}_2\text{O}} + A_{\text{ML}} K_1[\text{L}]}{1 + K_1[\text{L}]} \quad \text{B.23}$$

The equation has the same form as eq. 7.1 and can be used to determine the equilibrium constant, K_1 , from absorbance vs. concentration data.

B.3 Derivation of the rate equation for the reaction of the aqua/hydroxo complexes with monodentate ligands

The following reactions represent the reaction of an aqua or hydroxo complex with a monodentate ligand and the deprotonation of the aqua complex:





The overall rate for reactions B.25 and B.26 is given by the following reaction:

$$R = k_1[\text{MH}_2\text{O}][\text{L}] + k_2[\text{MOH}][\text{L}] - k_{-1}[\text{ML}] - k_{-2}[\text{ML}][\text{OH}^-] \quad \text{B.27}$$

The total concentration of the metal species in the solution is given by the following equation:

$$[\text{M}]_{\text{T}} = [\text{MH}_2\text{O}] + [\text{MOH}] \quad \text{B.28}$$

The following equation describes the acid dissociation constant in relation to the concentration of the different species in solution:

$$K_{a1} = \frac{[\text{MOH}][\text{H}^+]}{[\text{MH}_2\text{O}]} \quad \text{B.29}$$

Equations B.28 and B.29 can be written in terms of $[\text{MH}_2\text{O}]$:

$$[\text{M}]_{\text{T}} = [\text{MH}_2\text{O}] + \frac{K_{a1}[\text{MH}_2\text{O}]}{[\text{H}^+]} \quad \text{B.30}$$

Equations B.28 and B.29 can also be written in terms of $[\text{MOH}]$:

$$[\text{M}]_{\text{T}} = \frac{[\text{MOH}][\text{H}^+]}{K_{a1}} + [\text{MOH}] \quad \text{B.31}$$

Equations B.30 and B.31 can be rewritten as follows:

$$[\text{MH}_2\text{O}] = \frac{[\text{M}]_T}{1 + K_{a1}/[\text{H}^+]} \quad \text{B.32}$$

$$[\text{MOH}] = \frac{[\text{M}]_T}{1 + [\text{H}^+]/K_{a1}} \quad \text{B.33}$$

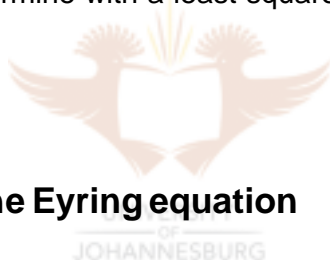
Substitute eq. B.32 and B.33 in eq. B.27

$$R = \frac{k_1[\text{M}]_T[\text{L}]}{1 + K_{a1}/[\text{H}^+]} + \frac{k_2[\text{M}]_T[\text{L}]}{1 + [\text{H}^+]/K_{a1}} - k_{-1}[\text{ML}] - k_{-2}[\text{ML}][\text{OH}^-] \quad \text{B.34}$$

Equation B.34 can be rewritten:

$$k_{\text{obs}} = \frac{k_1 + k_2 K_{a1}/[\text{H}^+]}{1 + K_{a1}/[\text{H}^+]} [\text{M}]_T [\text{L}] - k_{-1}[\text{ML}] - k_{-2}[\text{ML}][\text{OH}^-] \quad \text{B.35}$$

Equation B.35 is used to determine with a least squares fit of the k_{obs} vs. $[\text{L}]$ data the different rate constants.



B.4 Derivation of the Eyring equation

The transition state theory states that an activated complex or transition state is in equilibrium ($K_c^\ddagger =$ equilibrium constant) with the reagents before the reaction takes place and that the rate is given by the decomposition rate (k) of the activated complex to yield the products:



The rate for reaction B.36 is:

$$k = \frac{k_B T}{h} K_c^\ddagger \quad \text{B.37}$$

with $k_B =$ Boltzman's ($1.38066 \times 10^{-23} \text{ J K}^{-1}$) and $h =$ Planck's constants ($6.62608 \times 10^{-34} \text{ J s}$) respectively.

From basic thermodynamics it follows that:

$$K^\ddagger = e^{\frac{-\Delta G^{\ddagger 0}}{RT}} \quad \text{B.38}$$

with $\Delta G^{\ddagger 0}$ = standard free energy change and R = universal gas constant (8.3145 J K⁻¹ mol⁻¹).

With K_c^\ddagger being equal to K^\ddagger , the following equation, known as the Eyring equation, is obtained (exponential form):

$$k = T \frac{k_B}{h} e^{\left(\frac{\Delta S^\ddagger}{R}\right) - \left(\frac{\Delta H^\ddagger}{RT}\right)} \quad \text{B.39}$$

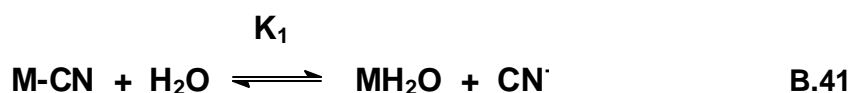
and in its natural logarithmic form:

$$\ln \frac{k}{T} = \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad \text{B.40}$$

Thus, a graph of $\ln \frac{k}{T}$ versus $\frac{1}{T}$ will have a slope of $-\frac{\Delta H^\ddagger}{R}$, with ΔH^\ddagger = standard enthalpy change of activation and the Y-intercept yielding $\frac{\Delta S^\ddagger}{R} + \ln \frac{k_B}{h}$, with ΔS^\ddagger = standard entropy change of activation.

B.5 Calculation of the concentration of the $[\text{MnN}(\text{CN})_5]^{3-}$ anion after dissociation in an aqueous solution.

The following reaction represents the dissociation of the $[\text{MnN}(\text{CN})_5]^{3-}$ anion in an aqueous solution to form the aqua complex:



B. GENERAL RATE AND EQUILIBRIUM EQUATIONS

The total concentration of the metal species in the solution is given by the following equation:

$$[M]_T = [MH_2O] + [MCN] \quad \text{B.42}$$

The following equation describes the equilibrium constant (K_e) in relation to the concentration of the different species in solution:

$$K_e = \frac{[MH_2O][CN^-]}{[MCN]} \quad \text{B.43}$$

Equations B.42 and B.43 can be written in terms of $[MCN]$:

$$[MCN] = \frac{[M]_T}{1 + K_e/[CN^-]} \quad \text{B.44}$$

Equations B.42 and B.43 can be written in terms of $[MH_2O]$:

$$[MH_2O] = \frac{[M]_T}{1 + [CN^-]/K_e} \quad \text{B.45}$$

The concentration of the different species in solution can be calculated using equations B.44 and B.45.