Key Equations for Reaction Kinetics

Fundamentals Lab

Aug 2020

1 Beer's Law

$$A = \varepsilon C \ell \tag{1}$$

Variables:

- A = absorbance
- C = Concentration of the absorbing agent
- ε = extinction coefficient (dependent on wavelength), also called absorptivity
- ℓ = path length (the width of the cuvette, typically 1 cm)

2 Rate Laws

We will start by assuming that the reaction is homogeneous since the reaction takes place entirely in the liquid phase. We can also assume that the reaction is irreversible. The rate law is *independent* of the type of reactor.

$$Rate\ of\ consumption\ of\ A = kC^mC^n \tag{2}$$

$$r_A = r_B = -kC_a{}^mC_b{}^n \tag{3}$$

3 Reaction Order

In the next lab in this series, you will determine the reaction order and rate constant. So, with this lab, you will develop your approach. The following equations will help you with this.

3.1 1^{st} Order

The following is for batch reactions, therefore:

$$\frac{-dC_A}{dt} = r_A \tag{4}$$

$$\frac{-dC_A}{dt} = kC_AC_{B0} \tag{5}$$

$$k' = kC_{B0} \tag{6}$$

$$\frac{dC_A}{dt} = -k'dt \tag{7}$$

$$\int_{C_{A0}}^{C_A} \frac{1}{C_A} dC_A = \int_0^t -k'dt \tag{8}$$

$$lnC_A - lnC_{A0} = -kt \tag{9}$$

$$lnC_A = -k\,t + lnC_{A0} \tag{10}$$

$$C_A = C_{A0} e^{-k^t t} \tag{11}$$

3.2 **2nd Order - 1 Species**

$$-rate_A = kC_A^2 \tag{12}$$

$$\frac{1}{C_A} = \frac{1}{C_{A0}} + kt \tag{13}$$

4 Arrhenius Equation

It is assumed that the rate constant, k is dependent only on temperature. The Arrhenius Equation is a model for how the rate constant changes with temperature. Just as a knowledge of the reaction order can aid you in knowing what parameters can be adjusted to help you manipulate the reaction rate, the Arrhenius Equation will show you how the temperature of the reaction will affect the rate. The Arrhenius equation is included on the equation sheet handout and is of the form:

$$k = Ae^{\frac{-E_a}{RT}} \tag{14}$$

It can also be linearized using the natural log:

$$\ln(k) = \frac{-E_a}{RT} + \ln(A) \tag{15}$$

5 Design Equations

In order to understand the basis of the reactor design equations, we first need to understand the mass balance equation:

$$In - Out + Generation = Accumulation \tag{16}$$

$$F_{A0} - F_A + \int_0^V r_A dV = \frac{dN_A}{dt} \tag{17}$$

5.1 Batch Reactors

Assumptions/Conditions:

- Well mixed
- Constant Volume

$$\frac{dN_A}{dt} = r_A V \tag{18}$$

5.2 Continuously Stirred Tank Reactor (CSTR)

Assumptions/Conditions:

- Well mixed
- Steady State

$$F_{A0} - F_A + r_A V = 0 \tag{19}$$

$$F_{A0} - F_A + r_A V = 0 \tag{20}$$

Substitute in conversion.

$$V = \frac{F_{A0} X}{-r_{A_{exit}}} \tag{21}$$

5.3 Plug Flow Reactor (PFR)

Assumptions/Conditions:

- Plug Flow (i.e. no radial variation)
- Steady State

$$\frac{dF_A}{dV} = r_A \tag{22}$$

Substitute in conversion.

$$F_{A0} \frac{dX_A}{dV} = -r_A \tag{23}$$

Rearrange and integrate to isolate volume.

$$V = F_{A0} \int_0^X \frac{dX}{-r_A} \tag{24}$$

6 Conversion

For a given reaction where: aA + bB –> cC + dD

$$X_A = \frac{C_{A0} - C_A}{C_{A0}} \quad (25)$$

Symbol	Initial	Change	End
A	C_{A0}	$-C_A X$	$C_A = C_{A0}(1 - X)$
B	C_{B0}	$-C_B X$	$C_B = C_{AO}(\Theta_B - \frac{b}{a}X)$
C	C_{C0}	$C_C X$	$C_C = C_{AO}(\Theta_C + \frac{c}{a}X)$
D	C_{D0}	$C_D X$	$C_D = C_{AO}(\Theta_D + \frac{d}{a}X)$

Table 1: Conversion Table for Concentration C

$$\Theta_i = \frac{C_{i0}}{C_{A0}} \, or \, \frac{N_{i0}}{N_{A0}} \, or \, \frac{F_{i0}}{F_{A0}} \quad (26)$$

Symbol	Initial	Change	End
A	N_{A0}	$-N_A X$	$N_A = N_{A0}(1 - X)$
B	N_{B0}	$-N_B X$	$N_B = N_{AO}(\Theta_B - \frac{b}{a}X)$
C	N_{C0}	$N_C X$	$N_C = N_{AO}(\Theta_C + \frac{c}{a}X)$
D	N_{D0}	$N_D X$	$N_D = N_{AO}(\Theta_D + \frac{d}{a}X)$

Table 2: Conversion Table for Moles (N)

Symbol	Initial	Change	End
A	F_{A0}	$-F_A X$	$F_A = F_{A0}(1 - X)$
B	F_{B0}	$-F_B X$	$F_B = F_{AO}(\Theta_B - \frac{b}{a}X)$
C	F_{C0}	$F_C X$	$F_C = F_{AO}(\Theta_C + \frac{c}{a}X)$
D	F_{D0}	$F_D X$	$F_D = F_{AO}(\Theta_D + \frac{d}{a}X)$

Table 3: Conversion Table for Moles/Min (F)