KINETICS

Kinetics are related to stoichiometry: rate at which reactants are consumed is related to the proportion(s) in which reactants combine to form products.

For calculation purposed, stoichiometries are converted to equations. Assuming a mass (or COD) based stoichiometry with a sign convention that

Coefficient for a reactant is negative (-), and

Coefficient for a product is positive (+)

Then state conservation of mass in a reaction:

$$(-1)A_1 + (-\Psi_2)A_2 + \ldots + (-\Psi_k)A_k + (\Psi_{k+1})A_{k+1} + \ldots + (\Psi_m)A_m = 0$$

Define an overall reaction rate, r and r_i = the rate of formation of A_i.

Such that

$$r = \frac{r_1}{-1} = \frac{r_2}{-\Psi_2} = \frac{r_k}{-\Psi_k} = \frac{r_{k+1}}{\Psi_{k+1}} = \frac{r_m}{\Psi_m}$$

Very useful for coupled reactions!

Example: Given COD-based stoichiometry and yield = 0.7 g-cell COD/g-COD consumed:

$$-1COD - (1-0.7)O_2 + 0.7COD\text{-cells} = 0$$

where substrate COD is A_1, oxygen is A_2, and cell-COD is A_3.

If cells are formed at a rate of 200 mg/L-hr (r_3), what is the rate of COD and oxygen consumption?

Calculate overall reaction rate, r, is calculated based on reference compound (cells)

$$r = r_3/\Psi_3 = 200 \text{ mg/l-hr}/0.7 = 286 \text{ g-COD/L-hr}$$

and

$$r_1 = -\Psi_1 * r = -1*286 \text{ g-COD/L-hr} = -286 \text{ g-COD/L-hr}$$

$$r_2 = -\Psi_2 * r = -(1-0.7)*286 \text{ g-COD/L-hr} = -86 \text{ g-}O_2\text{/L-hr} = 86 \text{ g-COD-}O_2\text{/L-hr}$$

Note that for the single growth stoichiometry, mass conservation is confirmed in the rate expressions:

$$r_1 + r_2 + r_3 = -286 + 86 + 200 \text{ g-COD/L-hr} = 0$$

Of interest are multiple reactions involving the multiple components, each with a varying set of stoichiometric components.

Generally:

Stoichiometries		**rate (j)**
$(-1)A_1 + \ldots + (-\Psi_{k,1})A_k + (\Psi_{k+1,1})A_{k+1} + \ldots + (\Psi_{m,1})A_m$	$= 0$	r_1
$(\Psi_{1,2})A_1 + \ldots + (-\Psi_{k,2})A_K + (\Psi_{k+1,2})A_{k+1} + \ldots + (1)A_m$	$= 0$	r_2
$(-\Psi_{1,3})A_1 + \ldots + (1)A_k + (\Psi_{k+1,3})A_{k+1} + \ldots + (-\Psi_{m,3})A_m$	$= 0$	r_3
•		•
•		•
•		•
$(-1)A_1 + \ldots + (-\Psi_{k,n})A_k + (-\Psi_{k+1,N})A_{k+1} + + \ldots + (\Psi_{m,N})A_m$	$= 0$	r_n

Note that A_i can be products in some reactions and reactant in others, as long as coefficients reflect this.

Characteristics:

For each reaction mass is conserved:

$$\sum_{i=1}^{\#\text{reactants}} \Psi_{i,j} = \sum_{i=\#\text{reactants}+1}^{\#\text{products}} \Psi_{i,j}$$

and expression for net formation rate of ith component over reactions $j = 1 \rightarrow n$ is r_i:

$$\text{overall formation / consumption rate for } i = r_i = \sum_{j=1}^{n} \Psi_{i,j} * r_j$$