KINETICS AND STOICHIOMETRY

Stoichiometries allow expressing rates of consumption or formation of any component during reactions in terms of the other components since stoichiometric coefficients reflect the proportion in which reaction components react.

First, convert stoichiometry (with arrow, $\rightarrow$) to equation, with = sign:

Sign convention is + for formation and – for consumption.

So for a mass-based stoichiometry, conservation of mass in a reaction with A_1 as the reference compound is expressed:

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

For any reaction, there is an overall reaction rate, r, usually related to the rate of formation or consumption of the reference compound such that for reaction (1):

$$r = \frac{r_1}{-1} = \frac{r_2}{-\varphi_2} = \ldots = \frac{r_k}{-\varphi_k} = \frac{r_{k+1}}{\varphi_{k+1}} = \ldots = \frac{r_m}{\varphi_m}$$

Example:

Given the COD stoichiometry and cell yield of 0.7 g-COD_{cells}/g-COD_S:

$$(-1)COD_S - (1-0.7)O_2 + (0.7)COD_{cells} = 0$$

And r_1 = rate of soluble COD consumption, r_2 = rate of O_2 consumption, and r_3 = rate of cell formation (mg/l-hr). If cells are produced at a rate of 200 mg/l-hr = r_3, what are the rates of soluble COD and oxygen consumption? Since we are using COD, substitute Y for Ψ:

$r = r_3/Y_3$ = 200 mg-COD_{cells}/l-hr/0.7mg-COD_{cells}/mg-COD_S = 286 COD/l-hr

$r_1 = -Y_1 * r$ = -1*286 mg-COD_S/l-hr = -286 mg-COD_S/l-hr

$r_2 = -Y_2 * r$ = -(1-0.7)mg-O_2/mg-COD*286 mg-COD/l-hr = -86 mg-O_2/l-hr

NOTE, you can express oxygen as COD and then r2 is a "COD formation" rate:

$r_2' = Y_2 * r$ = 86 mg-COD_{O2}/l-hr where r_2' is the rate of COD equivalents of oxygen produced.

For the COD stoichiometry:

$$\sum_{1=1}^{k} Y_i = \sum_{i=k+1}^{m} Y_i$$

-1+(1-0.7)+0.7 = 0 ✓

And the same is true for the rates when all terms are COD units:

$r_1 + r_2 + r_3 = 0$

-286 + 86 + 200 (mg-COD/l-hr) = 0 ✓

This format is especially useful when considering multiple reactions involving some or all of a set of components. For m components and n reactions:

Stoichiometry	rate
$(-1)A_1 + (-\Psi_{2,1}) A_2+\ldots+(-\Psi_{k,1}) A_k+\ldots+(\Psi_{k+1,1}) A_{k+1}+\ldots+(\Psi_{m,1}) A_m = 0$	r_1
$(\Psi_{1,2})A_1 + (-\Psi_{2,2}) A_2+\ldots+(-\Psi_{k,2}) A_k+\ldots+(\Psi_{k+1,2}) A_{k+1}+\ldots+(1) A_m = 0$	r_2
$(-\Psi_{1,3})A_1 + (\Psi_{2,3}) A_2+\ldots+(\Psi_{k,3}) A_k+\ldots+(\Psi_{k+1,3}) A_{k+1}+\ldots+(-\Psi_{m,3}) A_m = 0$	r_3
.	.
.	.
.	.
$(\Psi_{1,n})A_1 + (\Psi_{2,n}) A_2+\ldots+(-\Psi_{k,n}) A_k+\ldots+(\Psi_{k+1,n}) A_{k+1}+\ldots+(\Psi_{m,n}) A_m = 0$	r_n

Note that the ith component, A_i, can be a product or a reactant, depending on the reaction. For example, cells are a product in the growth reaction and a reactant in decay.

Then for each reaction, mass is conserved, as with

$$\sum_{1=1}^{k} \varphi_i = \sum_{i=k+1}^{m} \varphi_i$$

And the net rate of formation/consumption of the ith component, r_i, over all reactions, r_j for j = 1 → n, is:

$$r_i = \sum_{j=1}^{n} (\varphi_{i,j} * r_j)$$

Example:

Reaction 1 (cell growth on soluble COD):

$$(-1)COD_S - (1-0.7)O_2 + (0.7)COD_{cells} = 0$$

Reaction 2 (cell COD_{cells} decay and generation of soluble microbial products, COD_S, and debris, COD_{debris}) given 20% of decayed cells become debris and 80% become soluble COD:

$$(1-0.2)COD_S + (-1)COD_{cells} + 0.2COD_{debris} = 0$$

Then

For the coupled reactions 1 and 2, r_S = net rate of soluble COD_S consumption, r_O = net rate of soluble oxygen (as COD) consumption, r_{XB} = net rate of cell formation, and r_{XD} = net rate of debris formation. (all units mg-COD/l-hr)

$r_S = (-1)*r_1 + (1-0.2)*r_2$
$r_O = (1-0.7)r_1$ (as COD instead of O2)
$r_{XB} = (0.7)*r_1 - 1*r_2$
$r_{XD} = 0.2*r_2$

4 equations, 6 unknowns, need two values to solve:
Given r_O = 300 mg-COD_O/l-hr, and r_{XB} = 100 mg-COD_{cells}/l-hr, find r_S, r_{XD}, r_1 and r_2.

Solution:

$r_1 = r_O*(1-0.7) = 300/0.3 = 1{,}000$ mg-COD/l-hr
$r_2 = -1*r_{XB} + 0.7*r_1 = -100 + 700 = 600$ mg-COD/l-hr
$r_{XD} = 0.2*600 = 120$ mg-COD/l-hr
$r_S = -1000 + 0.8*600 = -520$ mg-COD/l-hr