

Kinetics and Reactor Design HW6

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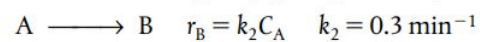
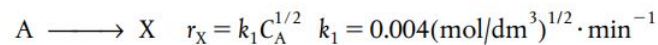
Assigned: March 8, 2023

Due: March 23, 2023

1 Problem Statement

1.1 P8-4_A (a, b)

P8-4_A Consider the following system of gas-phase reactions:



B is the desired product, and X and Y are foul pollutants that are expensive to get rid of. The specific reaction rates are at 27°C. The reaction system is to be operated at 27°C and 4 atm. Pure A enters the system at a volumetric flow rate of 10 dm³/min.

(a) Sketch the instantaneous selectivities ($S_{B/X}$, $S_{B/Y}$, and $S_{B/XY} = r_B/(r_X + r_Y)$) as a function of the concentration of C_A .

(b) Consider a series of reactors. What should be the volume of the first reactor?

Figure 1

1.2 P8-7_C (b, c)

P8-7_C Reactor selection and operating conditions. For each of the following sets of reactions, describe your reactor system and conditions to maximize the selectivity to D. Make sketches where necessary to support your choices. The rates are in (mol/dm³ · s), and concentrations are in (mol/dm³).

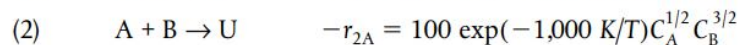
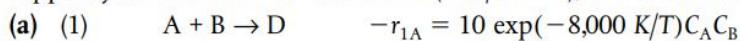


Figure 2

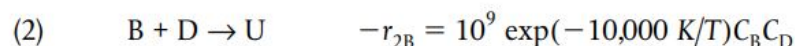
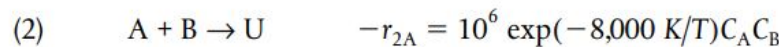
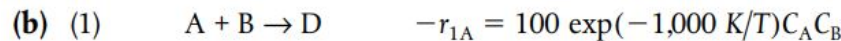
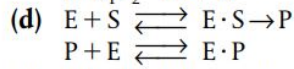
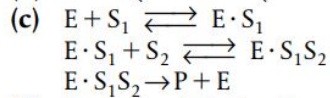
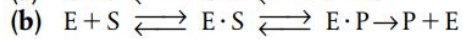
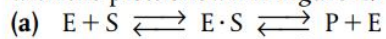


Figure 3

1.3 P9-8_B (a, b, d)

P9-8_B Derive the rate laws for the following enzymatic reactions and sketch and compare, where possible, with the plots shown in Figure E9-2.1.



(e) Which of the reactions (a) through (d), if any, lend themselves to analysis by a Lineweaver–Burk plot?

Figure 4

2 Problem Solution

2.1 P8-4_A (a, b)

a) $S_{B/X}$: this boils down to $\frac{k_2 C_A^{1/2}}{k_1}$. $S_{B/Y}$ boils down to $\frac{k_2}{k_3 C_A}$. $S_{B/XY}$ boils down to $\frac{r_B}{r_X + r_Y} = \frac{k_2 C_A}{k_1 C_A^{1/2} + k_3 C_A^2}$. We know the k values so we can plot all of these as a function of C_A . Here are the corresponding graphs:

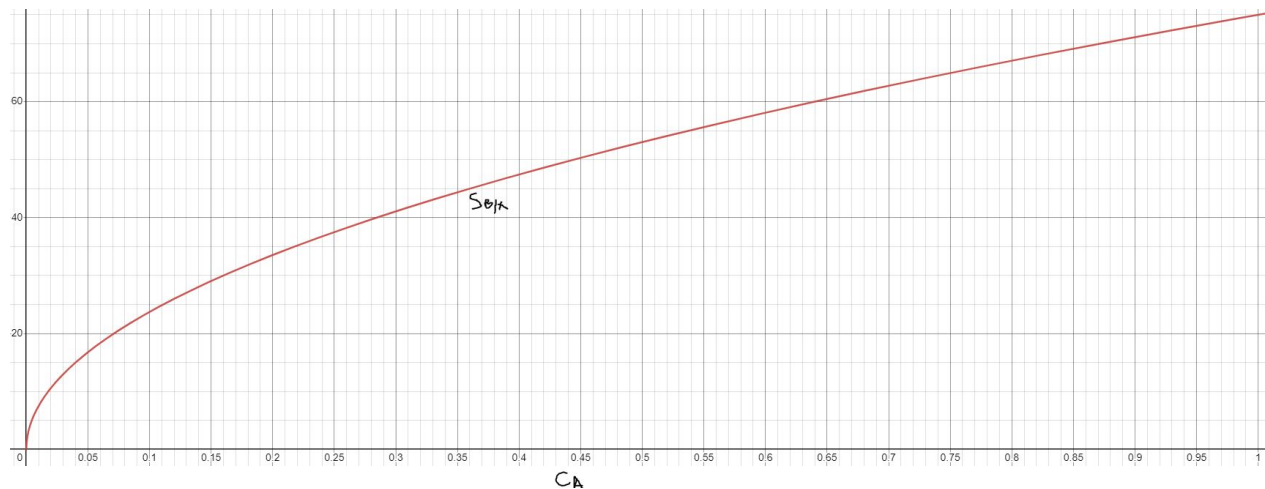


Figure 5: $S_{B/X}$

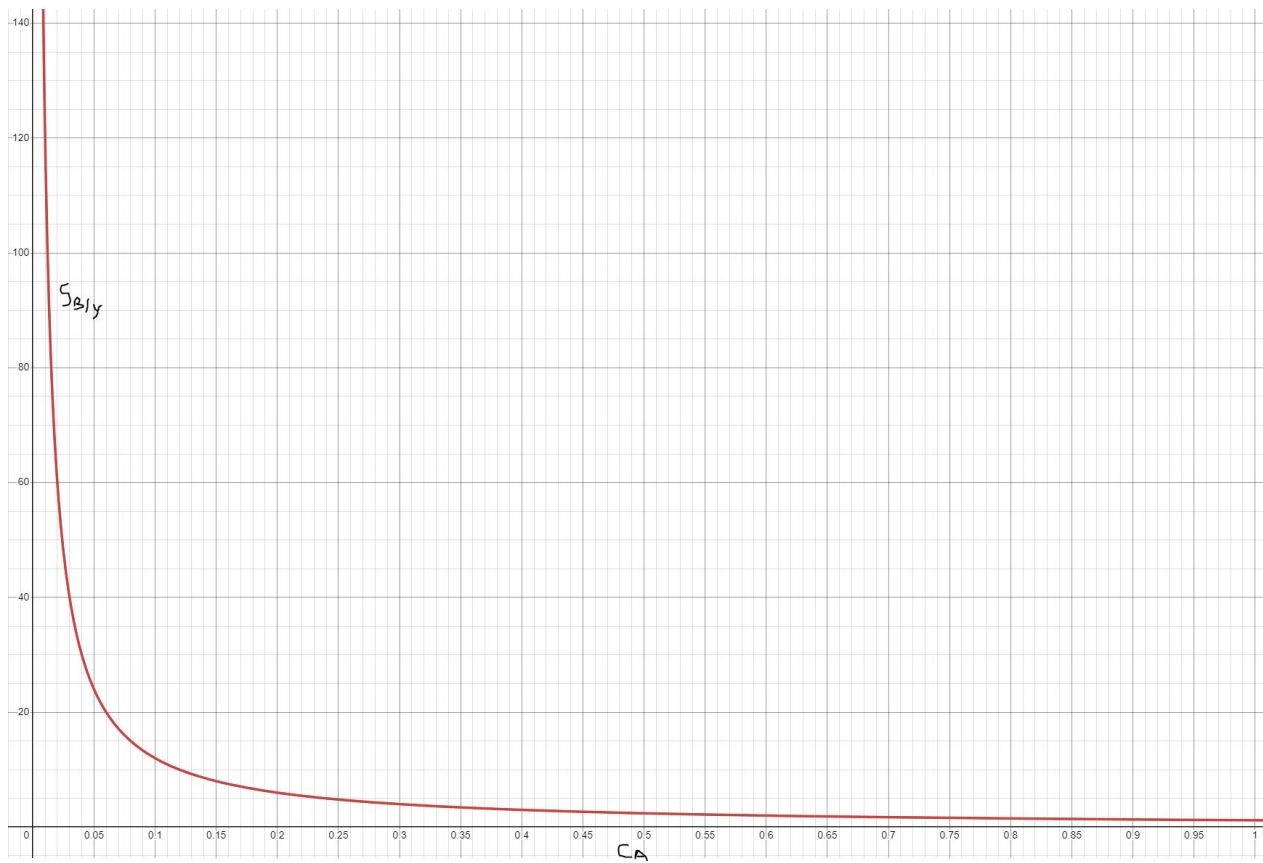


Figure 6: $S_{B/Y}$

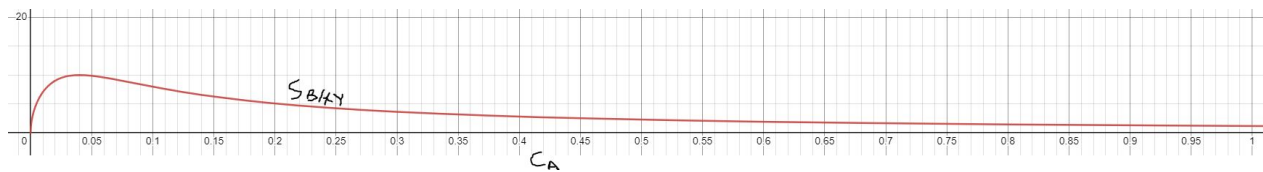


Figure 7: $S_{B/XY}$

b) Goal is to maximize $S_{B/XY}$, which according to the graph peaks at 10, at C_A of 0.04. Therefore we need a CSTR with exit C_A of 0.04 mol/dm³. We're given temperature and pressure - $C_{A0} = \frac{P_0}{RT} = 0.162$ mol/dm³. $-r_A = r_x + r_B + r_Y$ and -

$$V = \frac{\nu_0(C_{A0} - C_A)}{-r_A} \quad (1)$$

Solving for V using 0.04 as C_A yields 92.4 dm³.

2.2 P8-7_C (b, c)

b) $S_{DU} = \frac{r_D}{r_U}$. The $C_A C_{BS}$ cancel out so we're left with an expression with temperature as the main variable.

$$S_{DU} = \frac{e^{-1000K/T}}{10^4 e^{-8000K/T}} \quad (2)$$

S_{DU} increases a lot at lower temperatures - so keep temperatures low. c) $S_{DU} = \frac{r_{1A}}{r_{2A}}$. C_{BS} cancel out.

$$S_{DU} = \frac{e^{-8000K/T} C_A}{10^8 e^{-10000K/T} C_D} \quad (3)$$

Once again, temperature should be kept low to maximize S_{DU} . We also need to keep C_D low - we can achieve this using a membrane reactor, and keep C_A high (perhaps we can have a semipermeable membrane thru which A enters and D leaves?).

2.3 P9-8_B (a, b, d)

a) We need to apply PSSH to the complex ES.

$$k_1[E][S] - k_2[ES] - k_3[ES] + k_4[P][E] = 0 \quad (4)$$

$$[ES] = \left(\frac{k_1[S] + k_4[P]}{k_2 + k_3} \right) [E] \quad (5)$$

$$r_P = -r_S = k_3[ES] - k_4[P][E] \quad (6)$$

$$r_P = -r_S = \left(\frac{k_3 k_1 [S] - k_3 k_4 [P]}{k_2 + k_1} \right) [E] \quad (7)$$

$$[E_T] = [E] + [ES] = \left(\frac{k_2 + k_3 + k_1[S] + k_4[P]}{k_2 + k_3} \right) [E] \quad (8)$$

$$k_e = \frac{k_1 k_3}{k_2 k_4} \quad (9)$$

$$r_P = \frac{k_1 k_3 \left([S] - \frac{[P]}{k_e} \right)}{k_2 + k_3 + k_1[S] + k_4[P]} \quad (10)$$

b) Similar to last problem but there's a k_5 .

$$E_T = E + ES + EP \quad (11)$$

$$r_{ES} = k_1[E][S] - k_2[ES] - k_3[ES] + k_4[EP] \quad (12)$$

$$[EP] = \frac{k_3[ES]}{k_4 + k_5} \quad (13)$$

$$r_P = k_5[EP] = \frac{k_3 k_5 [ES]}{k_4 + k_5} \quad (14)$$

$$[ES] = \frac{k_1[S][E_T]}{1 + \frac{k_3}{k_4 + k_5}} = \frac{k_1[S]}{1 + \frac{k_3}{k_4 + k_5}} \left(k_1[S] + k_2 + k_3 - \frac{k_4 k_3}{k_4 + k_5} \right) \quad (15)$$

$$r_P = \frac{k_1 k_3 k_5 [S] [E_T]}{(k_3 + k_4 + k_5) k_1 [S] + k_2 k_4 + k_3 k_5} \quad (16)$$

d) PSSH again:

$$r_{[ES]} = 0 = k_1 [E] [S] - k_2 [ES] - k_3 [ES] \quad (17)$$

$$[ES] = \frac{k_1 [S] [E]}{k_2 + k_3} \quad (18)$$

$$r_{[EP]} = 0 = k_4 [E] [P] - k_5 [EP] \quad (19)$$

$$[EP] = \frac{k_4 [E] [P]}{k_5} \quad (20)$$

$$r_P = k_3 [ES] - k_4 [E] [P] + k_5 [EP] \quad (21)$$

$$r_P = \frac{k_1 k_3 [S] [E]}{k_2 + k_3} \quad (22)$$

$$[E_T] = [E] + [ES] + [EP] \quad (23)$$

$$[E_T] = [E] \left[1 + \frac{k_1 [S]}{k_2 + k_3} + \frac{k_4 [P]}{k_5} \right] \quad (24)$$

$$r_P = \frac{k_1 k_3 [S] [E_T]}{(k_2 + k_3) \left[1 + \frac{k_1 [S]}{k_2 + k_3} + \frac{k_4 [P]}{k_5} \right]} \quad (25)$$

We can algebraically manipulate the fraction to get rid of k_1 in the numerator and thus end up with 3 terms in the denominator:

$$\frac{k_2 + k_3}{k_1}; [S]; \frac{k_4 (k_2 + k_3) [P]}{k_1 k_5} \quad (26)$$

$k_3 [E_T]$ is V_{max} , the first denominator term is Michaelis-Menten constant K_M , third denominator term can be lumped into $K_P [P]$. So result:

$$r_P = \frac{V_{max} [S]}{K_M + [S] + K_P [P]} \quad (27)$$