

SOLNS - EXAM 1

1. (20 pts) Researchers at the Pass Gas Institute are interested in the reaction mechanism for the conversion of NO to NO₂ in oxygen.

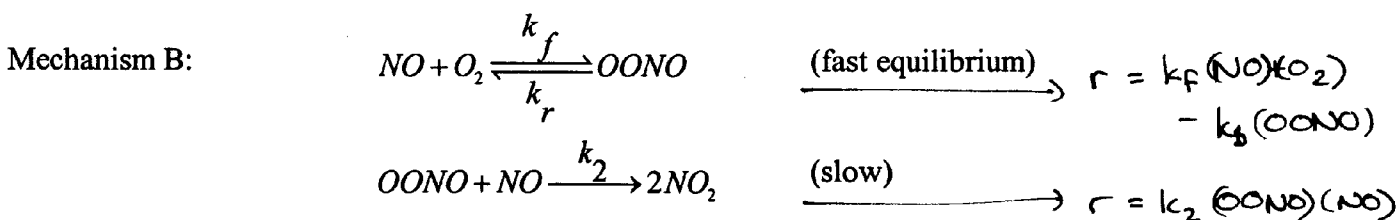
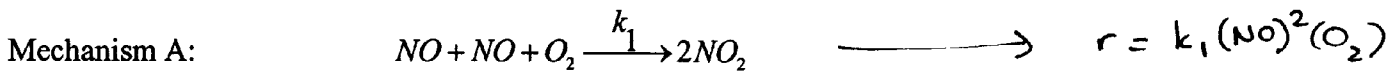
The overall reaction is:



and the experimentally determined rate law is:

$$r = k_{\text{obs}} [\text{NO}]^2 [\text{O}_2]$$

Two elementary reaction mechanisms are proposed:



a) Show that BOTH mechanisms agree with the experimentally determined form of the rate law by deriving an expression for r_{NO_2} .

Show how k_{obs} relates to the actual rate constants in each mechanism. Assume rate constants are defined with respect to the overall reaction rate for each step.

$= \frac{r_{\text{NO}_2}}{+2}$ Mech A: $r_{\text{NO}_2} = 2k_1 (\text{NO})^2 (\text{O}_2)$ k_{obs} is w.r.t r

$r = k_1 (\text{NO})^2 (\text{O}_2) \therefore k_{\text{obs}} = k_1$

Mech B: $r_{\text{NO}_2} = 2k_2 (\text{OONO})(\text{NO})$

QES: $\frac{k_f}{k_b} = \frac{(\text{OONO})}{(\text{NO})(\text{O}_2)} \longrightarrow (\text{OONO}) = \frac{k_f}{k_b} (\text{NO})(\text{O}_2)$

(fast equil)

Sub into $r_{\text{NO}_2} = 2k_2 \left(\frac{k_f}{k_b} (\text{NO})(\text{O}_2) \right) (\text{NO}) = \frac{2k_2 k_f}{k_b} (\text{NO})^2 (\text{O}_2)$

$r = \frac{k_2 k_f}{k_b} (\text{NO})^2 (\text{O}_2) \therefore k_{\text{obs}} = \frac{k_2 k_f}{k_b}$

b) Is one mechanism more likely than the other? If so, why?

B more likely than A

↑ termolecular rxn step
less likely

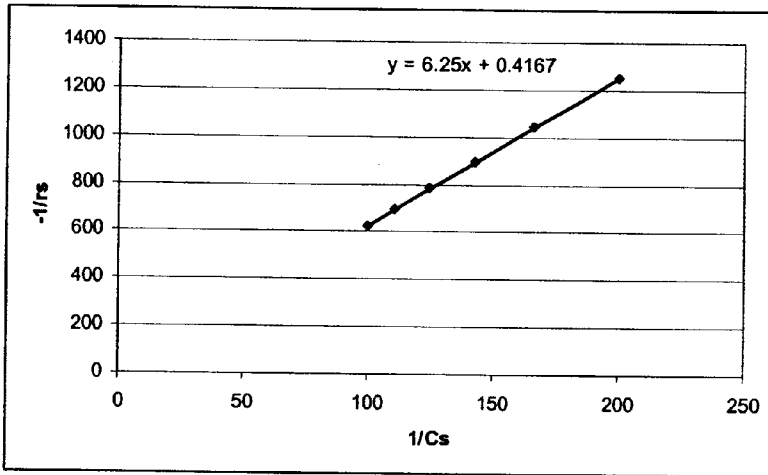
↑ all bimolecular rxn steps

2. (36 pts) Sonoma Shams Vineyard has patented a continuous process for the fermentation of wine in which yeast can be assumed to act as an enzyme to convert glucose (S) to ethanol:



The reaction rate data, which follow Michaelis-Menton kinetics, are below, along with some design parameters of the reactor, a PFR.

$C_{S0} = 0.01 \text{ moles/dm}^3$
 $C_{sf} = 0.005 \text{ moles/dm}^3$
 $v_0 = 2 \text{ dm}^3/\text{min}$
 $0.24 \text{ dm}^2 = \text{cross-sectional area of PFR}$



$$-r_s = \frac{V_{max} C_s}{C_s + K_m}$$

$$\Rightarrow \frac{1}{-r_s} = \frac{K_m}{V_{max} C_s} \frac{1}{C_s} + \frac{1}{V_{max}}$$

SLOPE b-intercept

The vine keeper, Frank, wants to install a small tap in the PFR so that he can enjoy some wine with his lunch break. Unfortunately, Frank is borderline diabetic and concentrations of glucose greater than 0.005 moles/L will cause him health problems.

a) Calculate the Michaelis constant, K_m , for this reaction. What simplification can you make to the reaction rate expression based on this value of K_m ? Write the simplified form of the rate expression.

From plot $y = \underbrace{6.25}_\frac{K_m}{V_{max}} x + \underbrace{0.4167}_\frac{1}{V_{max}} \rightarrow V_{max} = 2.40$

Using V_{max} $\frac{K_m}{2.40} = 6.25 \rightarrow K_m = 15 \frac{\text{mol}}{\text{dm}^3}$

$K_m \gg C_s = 0.01$ @ most

$$\therefore -r_s = \frac{V_{max} C_s}{\underset{\text{neglect}}{C_s + K_m}} = \frac{V_{max}}{K_m} C_s = \left(\frac{1}{6.25}\right) C_s = 0.16 C_s$$

b) Using the simplification from part a) calculate at what length down the reactor Frank should place the tap.

$$\frac{dF_S}{dV} = r_S = -0.14 C_S = -0.16 \frac{F_S}{N_0}$$

liquid phase!
 $N = N_0$

$$\int_{F_{S0}}^{F_S} \frac{1}{F_S} dF_S = \int_0^V \frac{-0.16 \frac{1}{\text{min}}}{2 \frac{\text{dm}^3}{\text{min}}} dV = -0.08 \frac{1}{\text{dm}^3} V = \ln \frac{F_S}{F_{S0}} = \ln \frac{0.01}{0.02}$$

$$F_S = C_S N_0 = (0.005 \frac{\text{mol}}{\text{dm}^3}) (2 \frac{\text{dm}^3}{\text{min}}) = 0.01 \frac{\text{mol}}{\text{min}}$$

$$F_{S0} = C_{S0} v_0 = (0.01 \frac{\text{mol}}{\text{dm}^3}) (2 \frac{\text{dm}^3}{\text{min}}) = 0.02 \frac{\text{mol}}{\text{min}}$$

$$V = \frac{\ln 0.5}{-0.08} \text{ dm}^3$$

$$V = 8.7 \text{ dm}^3$$

$$V = (A_{\text{sec}})(\text{length}) = (0.24 \text{ dm}^2)(\text{length}) = 8.7 \text{ dm}^3$$

$$\boxed{\text{length} = 36.25 \text{ dm}}$$

3. (30 pts) Most gases can be assumed to behave ideally, with a compressibility factor, Z , equal to 1:

$$Z = \frac{PV}{nRT} = 1$$

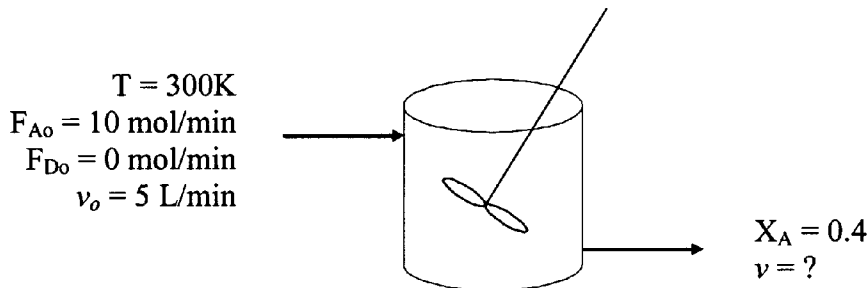
However, some gases exhibit non-ideal behavior and must be described by more complex equations of state. For example, the 1st-order virial expansion can be written as

$$Z = \frac{PV}{nRT} = 1 + \frac{BP}{RT}$$

where B is the 1st-order virial coefficient.

The following reaction is taking place in a CSTR: $A \rightarrow 3D$

Pure A can be treated as an ideal gas, but the conversion of A to D results in a GAS MIXTURE that can better be described by the 1st-order virial expansion with $B = -0.4$ L/mol. Given the following reactor design scheme, calculate the volumetric flow rate, v , out of the CSTR. Assume isobaric and isothermal reactor conditions, and steady-state operation. (Use $R = 0.0821$ L atm / mol K)



Multiple variations of the calculation but all involve recognizing 2 things: inlet of Pure A is IDEAL & outlet MIXTURE is NON-IDEAL

Use Inlet to calculate P: Pure A $PV = nRT \Rightarrow P_0 = \frac{n_0 RT_0}{V_0}$

iso P = P₀
iso T = T₀

$P_0 = 49.26 \text{ atm} \leftarrow \frac{10 \frac{\text{mol}}{\text{min}} (0.0821) (300 \text{ K})}{5 \frac{\text{L}}{\text{min}} \frac{\text{L atm}}{\text{mol K}}} = P_0 = \frac{F_{T_0} RT_0}{V_0}$

now for outlet:

$\frac{PV}{n_r RT} = 1 + \frac{BP}{RT} \Rightarrow \frac{V}{n_r} = \frac{1}{C_T} = \frac{V}{F_T} = \frac{RT}{P} \left(1 + \frac{BP}{RT} \right)$

$V = F_T \frac{RT}{P} \left(1 + \frac{BP}{RT} \right) = F_{A0} (1 + 2X_A) \frac{RT}{P} \left(1 + \frac{BP}{RT} \right)$
 $= 10 \frac{\text{mol}}{\text{min}} (1 + 2(0.4)) \frac{(0.0821 \frac{\text{L atm}}{\text{mol K}}) (300 \text{ K})}{49.26 \text{ atm}} \left(1 + \frac{(-0.42 \text{ atm}) (0.0821 \frac{\text{L atm}}{\text{mol K}})}{300 \text{ K}} \right)$

A $\frac{I_{ni}}{F_{A0}} = \frac{\text{Remain}}{F_{A0}(1-X_A)}$

B $0 = \frac{3F_{A0} X_A}{F_T = F_{A0}(1+2X_A)}$

$V = 1.8 \frac{\text{L}}{\text{min}}$

a) In your own words, describe the two approaches for deriving rate expressions from reaction mechanisms.

Rate limiting Step (RLS): assume 1 step slow that determines whole rxn rate
 • other steps fast equil (QES)

Pseudo-SS Hypothesis (PSSH): rate of change of an intermediate is approximately zero ($\frac{dI}{dt} = 0$)

b) The two basic ideal flow reactors are a CSTR and a PFR. Describe the main features/differences of each.

CSTR - well mixed throughout, outlet = reactor conditions
 flow reactor (usually SS)

PFR - no axial mixing, perfect radial mixing
 flow reactor (usually SS)
 difficult T control, high conversion/vol

