SOLNS - EXAM 1

1. (20 pts) Researchers at the Pass Gas Institute are interested in the reaction mechanism for the conversion of NO to NO_2 in oxygen.

The overall reaction is: **$2NO + O_2 \rightarrow 2NO_2$**

and the experimentally determined rate law is: **$r = k_{obs} [NO]^2 [O_2]$**

Two elementary reaction mechanisms are proposed:

Mechanism A: $NO + NO + O_2 \xrightarrow{k_1} 2NO_2$ $\longrightarrow$ $r = k_1 (NO)^2 (O_2)$

Mechanism B:

$NO + O_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} OONO$ (fast equilibrium) $\longrightarrow$ $r = k_f (NO)(O_2) - k_b (OONO)$

$OONO + NO \xrightarrow{k_2} 2NO_2$ (slow) $\longrightarrow$ $r = k_2 (OONO)(NO)$

a) Show that BOTH mechanisms agree with the experimentally determined form of the rate law by deriving an expression for r_{NO2}.

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.

$= \frac{r_{NO_2}}{+2}$

Mech A: $r_{NO_2} = 2 k_1 (NO)^2 (O_2)$ k_{obs} is W.R.T r

$r = k_1 (NO)^2 (O_2)$ $\therefore k_{obs} = k_1$

Mech B: $r_{NO_2} = 2 k_2 (OONO)(NO)$

QES: (fast equil) $\frac{k_f}{k_b} = \frac{(OONO)}{(NO)(O_2)} \longrightarrow (OONO) = \frac{k_f}{k_b} (NO)(O_2)$

Sub into $r_{NO_2} = 2 k_2 \left(\frac{k_f}{k_b} (NO)(O_2) \right)(NO) = \frac{2k_2 k_f}{k_b} (NO)^2 (O_2)$

$r = \frac{k_2 k_f}{k_b} (NO)^2 (O_2)$ $\therefore k_{obs} = \frac{k_2 k_f}{k_b}$

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

B more likely than A

all bimolecular rxn steps

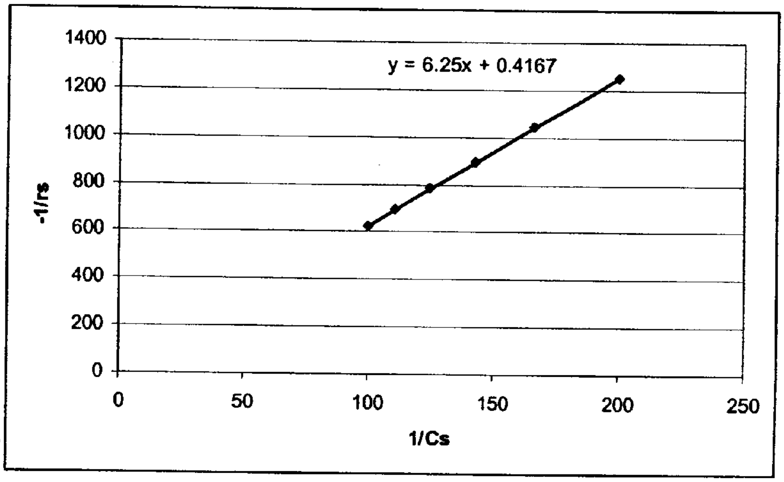
termolecular rxn step less likely

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:

$$E + C_6H_{12}O_6 \rightarrow 2CO_2 + 2C_2H_5OH + E$$

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

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



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

$$\Rightarrow \frac{1}{-r_s} = \underbrace{\frac{K_m}{V_{max}}}_{\text{SLOPE}}\frac{1}{C_s} + \underbrace{\frac{1}{V_{max}}}_{\text{b-intercept}}$$

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 $\quad y = \underbrace{6.25}_{\frac{K_m}{V_{max}}}x + \underbrace{0.4167}_{\frac{1}{V_{max}}} \longrightarrow V_{max} = 2.40$

Using V_{max} $\quad \frac{K_m}{2.40} = 6.25 \longrightarrow \boxed{K_m = 15\ \frac{mol}{dm^3}}$

$K_m >> C_s = 0.01$ @ most

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

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

liquid phase !
$\nu = \nu_o$

$$\frac{dF_S}{dV} = r_S = -0.16\, C_S = -0.16 \frac{F_S}{\nu_o}$$

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

$$F_S = C_S \nu_o = (0.005 \tfrac{mol}{dm^3})(2 \tfrac{dm^3}{min}) = 0.01 \tfrac{mol}{min}$$

$$F_{S0} = C_{S0} \nu_o = (0.01 \tfrac{mol}{dm^3})(2 \tfrac{dm^3}{min}) = 0.02 \tfrac{mol}{min}$$

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

$$V = 8.7\ dm^3$$

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

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

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

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

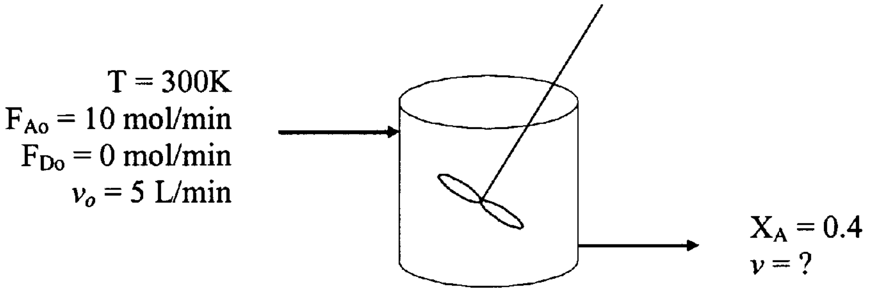
However, some gases exhibit non-ideal behavior and must be described by more complex equations of state. For example, the 1st-order virial expansion can be written as

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

where B is the 1st-order virial coefficient.

The following reaction is taking place in a CSTR: **A → 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 <u>IDEAL</u> & outlet MIXTURE is <u>NON-IDEAL</u>

Use Inlet to calculate P : Pure A $PV=nRT \Rightarrow P_o = \frac{n_{To}}{V_o} RT_o$

$P_o = C_{To} R T_o$

iso $P = P_o$
iso $T = T_o$

$$\boxed{P_o = 49.26 \text{ atm}} \Leftarrow \frac{10 \frac{mol}{min}}{5 \frac{L}{min}} (0.0821 \tfrac{L\,atm}{mol\,K})(300K) = P_o = \frac{F_{To}}{\nu_o} RT_o$$

now for outlet:

$$\frac{PV}{n_T RT} = 1 + \frac{BP}{RT} \Longrightarrow \frac{V}{n_T} = \frac{1}{C_T} = \frac{\nu}{F_T} = \frac{RT}{P}\left(1 + \frac{BP}{RT}\right)$$

$$\nu = F_T \frac{RT}{P}\left(1 + \frac{BP}{RT}\right) = F_{A0}(1+2X_A)\frac{RT}{P}\left(1 + \frac{BP}{RT}\right)$$

$$= 10\frac{mol}{min}(1+2(0.4))\frac{(0.0821 \frac{L\,atm}{mol\,K})(300K)}{49.26\text{ atm}}\left(1 + \frac{(-0.4)P}{(0.0821 \frac{L\,atm}{mol\,K})T}\right)$$

49.26 atm

T=300K

	Ini.	Remain
A	F_{A0}	$F_{A0}(1-X_A)$
B	0	$3F_{A0}X_A$

$F_T = F_{A0}(1+2X_A)$

$$\boxed{\nu = 1.8 \frac{L}{min}}$$

4. Short Answer (24 pts, 6 pts each)

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 $\left(\frac{dI}{dt} = 0\right)$

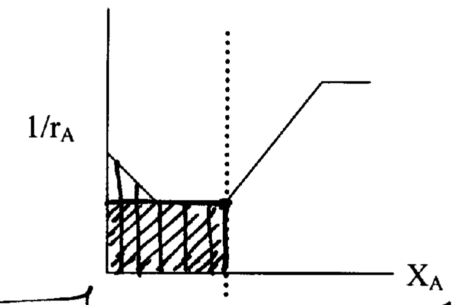
b) The two basic ideal flow reactors are a CSTR and a PFR. Describe the main features/differences of each.

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

c) The following rate vs. conversion data are determined experimentally. If you could use only one type of ideal flow reactor, which one would you select for the following situations and why? Assume the inlet to the reactor is pure.

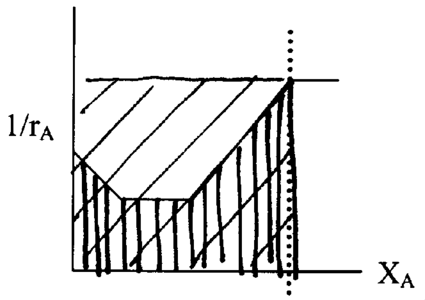
i) $X_A = 0.5$



▨ $\boxed{\text{CSTR}}$ < PFR ▥
area   area

$\therefore \frac{V_{CSTR}}{F_{A0}} < \frac{V_{PFR}}{F_{A0}}$

ii) $X_A = 0.8$



▨ CSTR > $\boxed{\text{PFR}}$ ▥
area   area

$\frac{V_{CSTR}}{F_{A0}} > \frac{V_{PFR}}{F_{A0}}$

d) Describe the physical meaning of the following parameters (as discussed in class): and.

i) δ $\frac{\text{change in moles}}{\text{mol of A reacted}}$
↗
limiting

ii) ε $\frac{\text{change in moles as as a result of complete conversion}}{\text{mol (total) fed to reactor}}$