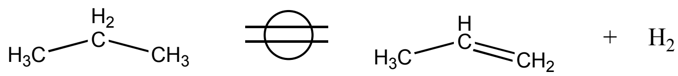
Chapter 1

Exercise 1:



propane (A) propylene (B) (C)

At equilibrium:

$$K_a = K_x K_\phi K_P = \left[\frac{X_B X_C}{X_A}\right]\left[\frac{\phi_B \phi_C}{\phi_A}\right]\left[\frac{P_{tot} P_{tot}}{P_{tot}}\right][1 \text{ atm}]^{-1} \quad (1)$$

Assuming ideal behavior,

$$K_a = \frac{P_B^o \cdot P_C^o}{P_A^o} = \frac{X_B P_{tot} \cdot X_C P_{tot}}{X_A P_{tot}} = \frac{X_B X_C}{X_A} \cdot P_{tot} \quad (2)$$

$$X_B = X_C \quad (3)$$

$$1 = X_A + X_B + X_C \quad (4)$$

Using equations (2), (3), and (4), solve for the three unknown mole fractions and find the fractional conversion of propane at each temperature.

$$f_A = 1 - X_A \quad (5)$$

Or an Alternate Solution:

Write a mole balance for the reaction.

(Where f_A = fractional conversion of propane)

	Initial Moles	Change in Moles	Final Moles
A	n_A^o	$-n_A^o f_A$	$n_A^o (1 - f_A)$
B	0	$n_A^o f_A$	$n_A^o (f_A)$
C	0	$n_A^o f_A$	$n_A^o (f_A)$
Total	n_A^o	$n_A^o f_A$	$n_A^o (1 + f_A)$

Express the mole fraction of each species in terms of f_A.

$$X_A = \frac{\text{(Moles of A)}}{\text{(Total Moles)}} = \frac{n_A^o(1-f_A)}{n_A^o(1+f_A)} = \frac{(1-f_A)}{(1+f_A)} \qquad (6)$$

$$X_B = \frac{f_A}{1+f_A} \qquad (7)$$

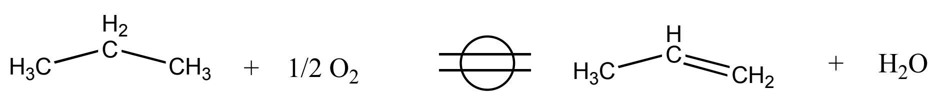
$$X_C = \frac{f_A}{1+f_A} \qquad (8)$$

Substitute equations (6), (7), and (8) into equation (2), above, and solve for fractional conversion (f_A).

$$K = \frac{f_A^2}{(1+f_A)(1-f_A)} \cdot P_{tot} \qquad (9)$$

	@ 400° C	@ 500° C	@ 600° C
Conversion (f_A)	0.0228	0.1012	0.3076

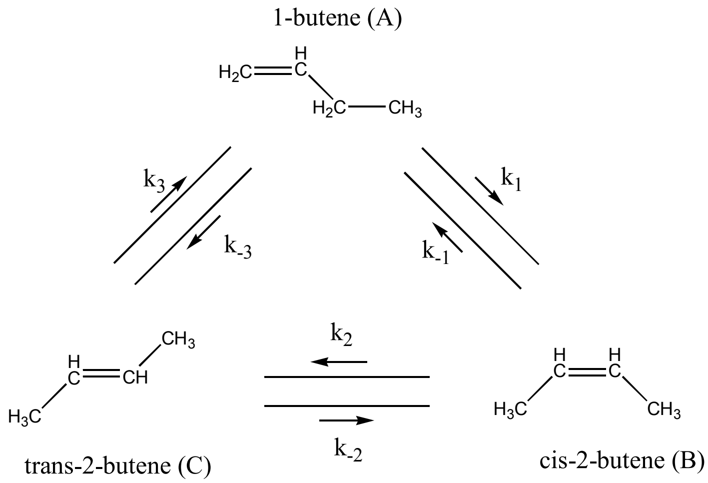
Exercise 2:



propane (A) (B) propene (C) (D)

Assume 100% conversion of propane at each temperature, because the equilibrium constants are so high. A major impediment is the oxidation of propane to CO_2 (not shown).

Exercise 3:



Part a)

Express the equilibrium constants for each step in terms of partial pressures.

$$K_{a1} = K_{P1} = \frac{P_B}{P_A} \tag{1}$$

$$K_{a2} = K_{P2} = \frac{P_C}{P_B} \tag{2}$$

$$K_{a3} = K_{P3} = \frac{P_A}{P_C} = \frac{P_A}{P_B} \cdot \frac{P_B}{P_C} \tag{3}$$

Rewrite equation (3) in terms of K_1 and K_2.

$$K_3 = \frac{1}{K_{P1}} \cdot \frac{1}{K_{P2}} \tag{4}$$

Therefore, $K_3 = 0.108$.

Part b)

Check the independence of the 3 reactions.

$$0 = \sum_{i=1}^{3} \upsilon_i \cdot A_i \quad \text{For all 3 equations.} \tag{5}$$

$$\begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} -1 & 1 & 0 \\ 0 & -1 & 1 \\ -1 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} A \\ B \\ C \end{bmatrix} \qquad \text{And} \qquad \text{Det(Matrix)} = (-1 \cdot -1) - (-1 \cdot 1) = 0$$

Therefore, all equations are not independent (i.e. only need 2 equations to solve).

Assuming a basis of 1 mole of 1-butene, write a mole balance for the system.

	Initial Moles	Change	Final Moles
A	1	$-\xi_1-\xi_3$	$1-\xi_1-\xi_3$
B	0	ξ_1	ξ_1
C	0	ξ_3	ξ_3
Total	1	0	1

Rewrite equations (1) and (3) in terms of ξ_1 and ξ_2.

$$K_{a1} = \frac{P_B}{P_A} = \frac{X_B P_{tot}}{X_A P_{tot}} = \frac{\xi_1}{1-\xi_1-\xi_3} \tag{6}$$

$$K_{a3} = \frac{P_C}{P_B} = \frac{\xi_3}{\xi_1} \tag{7}$$

Solving for ξ_1 and ξ_3 gives an equilibrium conversion of 1-butene = 0.932.

Mole fractions at equilibrium:

$X_{1\text{-butene}} = 0.068$
$X_{cis\text{-}2\text{-butene}} = 0.296$
$X_{trans\text{-}2\text{-butene}} = 0.636$

Exercise 4:

First, find K for each reaction from DG^o, using equation (1), assuming ideal behavior.

$$\ln(K) = \frac{-\Delta G^0}{R_g \cdot T} \tag{1}$$

Reaction	ΔG^0 (kJ mol^{-1})	K
1	14.85	0.078
2	10.42	0.167
3	15.06	0.075

Write a mole balance on the system of reactions, assuming a basis of 1 mole toluene.

	Initial Moles	Change	Final Moles
Toluene (A)	1	$-2\xi_1-2\xi_2-2\xi_3$	$1-2\xi_1-2\xi_2-2\xi_3$
Ortho-Xylene (B)	0	ξ_1	ξ_1
Meta-Xylene (C)	0	ξ_2	ξ_2
Para-Xylene (D)	0	ξ_3	ξ_3
Benzene (E)	0	$\xi_1 + \xi_2 + \xi_3$	$\xi_1 + \xi_2 + \xi_3$
TOTAL	1	0	1

Express the equilibrium constants in terms of ξ_1, ξ_2, and ξ_3.

$$K_1 = \frac{X_B \cdot X_E}{(X_A)^2} = \frac{\xi_1(\xi_1 + \xi_2 + \xi_3)}{(1 - 2\xi_1 - 2\xi_2 - 2\xi_3)^2} \tag{2}$$

$$K_2 = \frac{\xi_2(\xi_1 + \xi_2 + \xi_3)}{(1 - 2\xi_1 - 2\xi_2 - 2\xi_3)^2} \tag{3}$$

$$K_3 = \frac{\xi_3(\xi_1 + \xi_2 + \xi_3)}{(1 - 2\xi_1 - 2\xi_2 - 2\xi_3)^2} \tag{4}$$

Solve for ξ_1, ξ_2, and ξ_3 and calculate the equilibrium compositions of each species.

The equilibrium mole fractions are:

Toluene = 0.470
Ortho-Xylene = 0.065
Meta-Xylene = 0.138
Para-Xylene = 0.062
Benzene = 0.265

Since para-xylene has a smaller kinetic diameter than either ortho- or meta-xylene, a shape selective catalyst that allows mostly para-xylene to diffuse out of it will shift the product distribution.

Exercise 5:

Part a)

Assuming a basis of 1 mole of feed, write an overall mole balance.

	Initial Moles	Change	Final Moles
Acetylene (A)	0.5	$-\xi_1$	$0.5 - \xi_1$
HCl (B)	0.5	$-\xi_1 - \xi_2$	$0.5 - \xi_1 - \xi_2$
Vinyl Chloride (C)	0	$\xi_1 - \xi_2$	$\xi_1 - \xi_2$
1,2 Dichloroethane (D)	0	ξ_2	ξ_2
TOTAL	1	$-\xi_1 - \xi_2$	$1 - \xi_1 - \xi_2$

Express the equilibrium constants in terms of ξ_1, ξ_2, and ξ_3.

For the reaction that forms vinyl chloride (C),

$$K_{a1} = K_{x1} K_{\phi 1} K_{P1} = \left[\frac{X_c}{X_A X_B}\right]\left[\frac{\bar{\phi}_c}{\bar{\phi}_A \bar{\phi}_B}\right]\left[\frac{P_{tot}}{P_{tot} P_{tot}}\right][1 \text{ atm}] \qquad (1)$$

Assuming ideal behavior,

$$K_{a1} = \frac{X_C}{X_A X_B} \cdot \frac{1}{P_{tot}} = \frac{(\xi_1 - \xi_2)(1 - \xi_1 - \xi_2)}{(0.5 - \xi_1)(0.5 - \xi_1 - \xi_2)} \cdot \frac{1}{5} \qquad (2)$$

Similarly for the reaction that forms 1,2 dichloroethane,

$$K_{a2} = \frac{X_D}{X_C X_B} \cdot \frac{1}{P_{tot}} = \frac{\xi_2 (1 - \xi_1 - \xi_2)}{(\xi_1 - \xi_2)(0.5 - \xi_1 - \xi_2)} \cdot \frac{1}{5} \qquad (3)$$

Solve for ξ_1, ξ_2, and ξ_3 and calculate the equilibrium compositions of each species.

$X_{\text{Acetylene}} = 0.012$
$X_{\text{HCl}} = 0.002$
$X_{\text{Vinyl chloride}} = 0.976$
$X_{\text{1,2 Dichloroethane}} = 0.010$

Find the fractional conversion of acetylene.

$$f_A^{eq} = 1 - \frac{n_A}{n_A^o} = 0.988 \qquad (4)$$

Part b)

Write another mole balance similar to part (a) but now add 9 moles of inert gas.

	Initial Moles	Change	Final Moles
Acetylene (A)	0.5	$-\xi_1$	$0.5 - \xi_1$

HCl (B)	0.5	$-\xi_1 - \xi_2$	$0.5 - \xi_1 - \xi_2$
Vinyl Chloride (C)	0	$\xi_1 - \xi_2$	$\xi_1 - \xi_2$
1,2 Dichloroethane (D)	0	ξ_2	ξ_2
Inert Gas (I)	9	0	9
TOTAL	10	$-\xi_1 - \xi_2$	$10 - \xi_1 - \xi_2$

Express the equilibrium constants in terms of ξ_1, ξ_2, and ξ_3.

$$K_{a1} = \frac{X_C}{X_A X_B} \cdot \frac{1}{P_{tot}} = \frac{(\xi_1 - \xi_2)(10 - \xi_1 - \xi_2)}{(0.5 - \xi_1)(0.5 - \xi_1 - \xi_2)} \cdot \frac{1}{5} \tag{5}$$

$$K_{a2} = \frac{X_D}{X_C X_B} \cdot \frac{1}{P_{tot}} = \frac{\xi_2 (10 - \xi_1 - \xi_2)}{(\xi_1 - \xi_2)(0.5 - \xi_1 - \xi_2)} \cdot \frac{1}{5} \tag{6}$$

Solve for ξ_1, ξ_2, and ξ_3 and calculate the equilibrium compositions of each species.

$X_{Acetylene} = 0.0014$
$X_{HCl} = 0.0012$
$X_{Vinyl\ Chloride} = 0.0510$
$X_{1,2\ Dichloroethane} = 0.0002$
$X_{Inert} = 0.946$

Find the fractional conversion of acetylene.

$$f_A^{eq} = 1 - \frac{n_A}{n_A^o} = 0.974 \tag{7}$$

Exercise 6:

Write the rate expression for the 2-propanol (P) reaction, rearrange, and integrate.

$$\frac{dn_P}{dt} = -k \cdot n_P \tag{1}$$

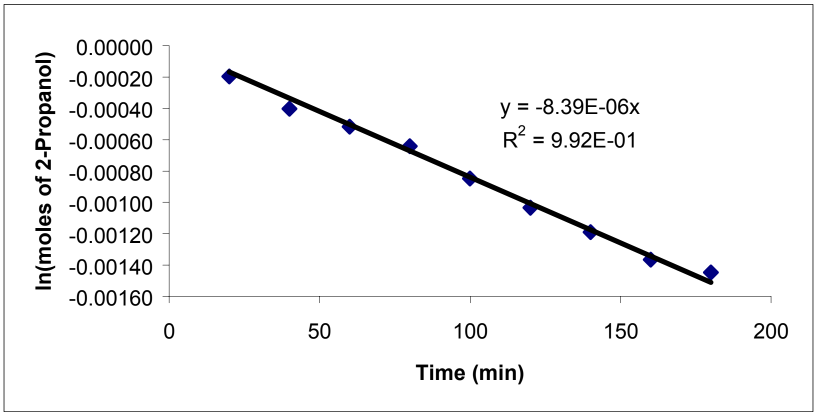
$$\int_{n_P^o}^{n_P} \frac{dn_P}{n_P} = -\int_0^t k \cdot dt \tag{2}$$

$$\ln\left(\frac{n_P}{n_P^o}\right) = -kt \tag{3}$$

Before plotting the data, convert $\frac{g_{\text{Acetone}}}{g_{\text{Propanol}}}$ to $\frac{n_P}{n_P^o}$.

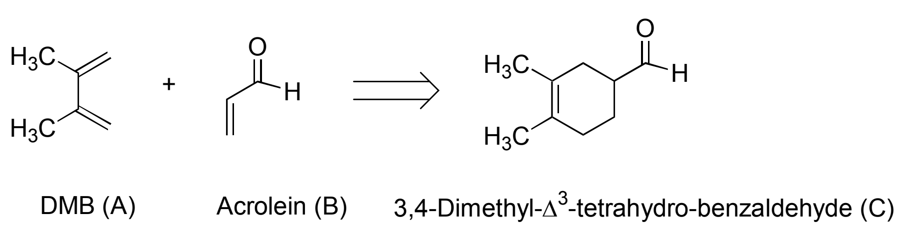
$$\frac{g_a}{g_P} \cdot \frac{60g_P}{1mol_P} \cdot \frac{1mol_a}{58g_a} = \frac{n_a}{n_P} \tag{4}$$

$$n_a = n_a^o + \left(\frac{-1}{1}\right)(n_P - n_P^o) \tag{5}$$



The first order rate constant (k) is the negative of the slope = 8.39×10^{-6} min^{-1}.

Exercise 7:



Assuming constant volume, write the second order rate equation for DMB.

$$\frac{dC_A}{dt} = -k \cdot C_A C_B \tag{1}$$

Now find C_B in terms of C_A.

$$C_B = C_B^o + \left(\frac{-1}{-1}\right)(C_A - C_A^o) \quad \text{And} \quad C_A^o = C_B^o \tag{2}$$

Therefore, $C_B = C_A$.

Rewrite the rate equation (equation (1)) in terms of f_A.

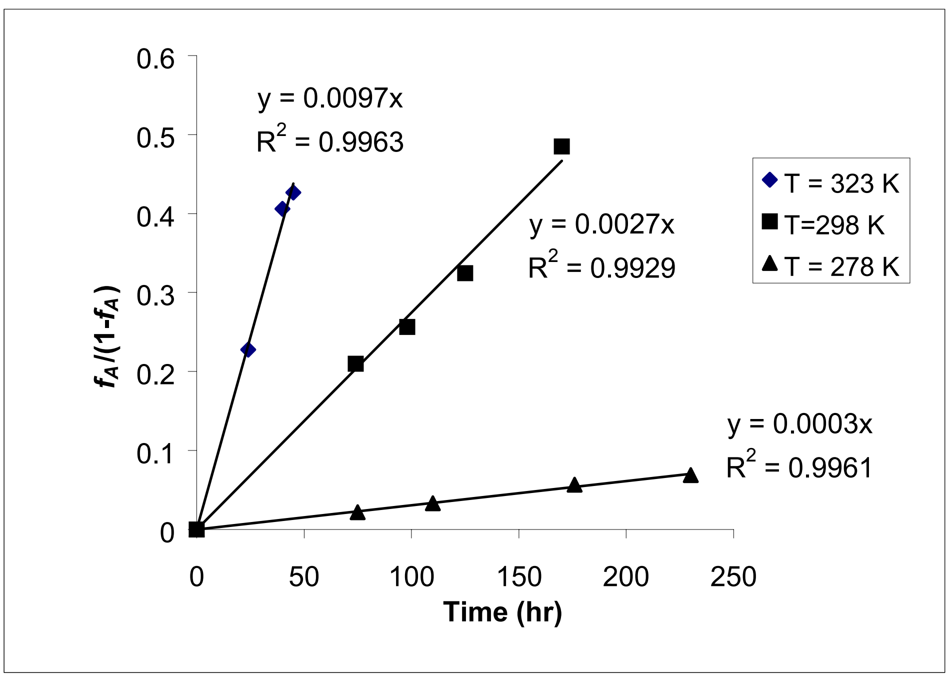
$$-C_A^o \frac{df_A}{dt} = -k(C_A^o)^2(1-f_A)^2 \tag{3}$$

$$\int_0^{f_A} \frac{df_A}{(1-f_A)^2} = \int_o^t kC_A^o \cdot dt \tag{4}$$

Solve this integral

$$\frac{f_A}{1-f_A} = kC_A^o t \tag{5}$$

Finally, plot $\frac{f_A}{1-f_A}$ vs. time at each temperature and find slope, kC_A^o.



Temperature (K)	Rate Constant (L mol^{-1} hr^{-1})
323	0.100
298	0.028
278	0.0033

Exercise 8:

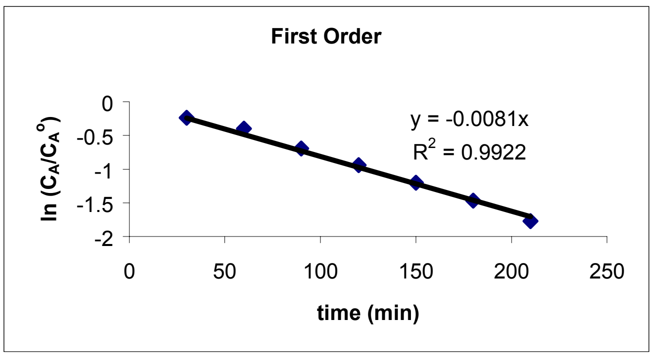
This reaction can be assumed to be of the form $A \longrightarrow$ Products.

Assuming the reaction to be 1st order, write the appropriate first order rate expression and integrate.

$$\frac{dC_A}{dt} = -kC_A \tag{3}$$

$$\ln\left(\frac{C_A}{C_A^o}\right) = -kt \tag{4}$$

Now a plot of $\ln\left(\frac{C_A}{C_A^o}\right)$ vs. time should be linear with a slope = -*k*.



Assuming $\frac{C_A}{C_A^o}$ is equivalent to relative absorbance, a plot of ln(relative adsorbance) vs. time should be linear with slope = -*k*.

The data appear first order with a rate constant, $k = 0.0081$ min^{-1}. Analogous attempts to fit zero and second order reaction rate experiments failed.

Exercise 9:

Express n_A and n_B in terms of fractional conversion of A (f_A).

$$n_A = n_A^o - n_A^o \cdot f_A \tag{1}$$
$$n_B = n_B^o - 2n_A^o \cdot f_A \tag{2}$$

For constant density (ρ), and constant volume (V), $\frac{n_i}{V}$ can be expressed as concentration (C_i).

$$C_A = C_A^o - C_A^o \cdot f_A \tag{3}$$

$$C_B = C_B^o - 2C_A^o \cdot f_A \qquad \text{And } \frac{C_B^o}{C_A^o} = 3 \text{ so,} \tag{4}$$

$$C_B = C_A^o(3 - 2f_A) \tag{5}$$

Substitute equations (3) and (5) into the given rate expression.

$$\frac{dC_A}{dt} = \frac{d(C_A^o - C_A^o \cdot f_A)}{dt} = -C_A^o \cdot \frac{df_A}{dt} \tag{6}$$

$$\frac{df_A}{dt} = \frac{kC_A C_B{}^2}{C_A^o} = kC_A^{o\,2}(1 - f_A)(3 - 2f_A)^2 \tag{7}$$

Separate variables and integrate.

$$\int_0^{0.5} \frac{df_A}{(1 - f_A)(3 - 2f_A)^2} = \int_0^{10} kC_A^{o\,2} \cdot dt \tag{8}$$

Solving for the rate constant (k) gives $k = 120 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$.

Exercise 10:

Calculate the total moles of gas initially in the system for N_2:H_2:He = 3:1:0, assuming ideal gas behavior.

$$P_{648K}^o = T_{648K}\left(\frac{P_{298K}^o}{T_{298K}}\right) \tag{1}$$

$$n_{tot}^o = \frac{P^o V}{R_g T^o} = 0.013 \text{ mol} \tag{2}$$

Write a gas phase mole balance.

	Initial Moles	Change	Final Moles
N_2	9.75×10^{-3}	$-\xi(t)$	$9.75 \times 10^{-3} - \xi(t)$
H_2	3.25×10^{-3}	$-3\xi(t)$	$3.25 \times 10^{-3} - 3\xi(t)$
He	0	0	0

NH_3	0	0	0
Total	0.013	$-4\xi(t)$	$0.013 - 4\xi(t)$

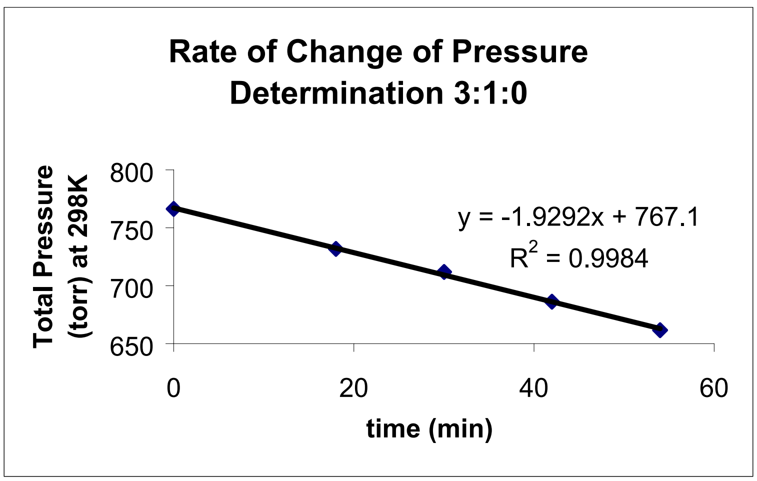
Derive the rate expression using the ideal gas law and express the rate in terms of $\frac{dP_{tot}}{dt}$.

$$P_{tot}V = n_{tot}R_gT \longrightarrow \frac{dn_{tot}}{dt} = \frac{V}{R_gT}\left(\frac{dP_{tot}}{dt}\right) \tag{3}$$

$$\frac{dn_{tot}}{dt} = -4\frac{d\xi}{dt} \quad \text{And} \quad \frac{dn_{N_2}}{dt} = -\frac{d\xi}{dt} \tag{4}$$

Therefore, $\frac{d\xi}{dt}$ is the rate of reaction, and $\frac{d\xi}{dt} = \frac{-V}{4R_gT}\left(\frac{dP_{tot}}{dt}\right)$. (5)

Plot Total Pressure vs. Time to find the rate of change in pressure (i.e. slope)



From the graph $\frac{dP_{tot}}{dt}$ = -1.9292 torr min^{-1}.

Repeat the same process for the other gas ratios and solve for $\frac{d\xi}{dt}$.

Ratio (N_2:H_2:He)	$\frac{dP_{tot}}{dt}$ (torr min^{-1})	$\frac{d\xi}{dt}$ (mol min^{-1})
3:1:0	-1.9292	8.17×10^{-6}
1:1:2	-0.8947	3.79×10^{-6}
1:3:0	-0.5668	2.40×10^{-6}

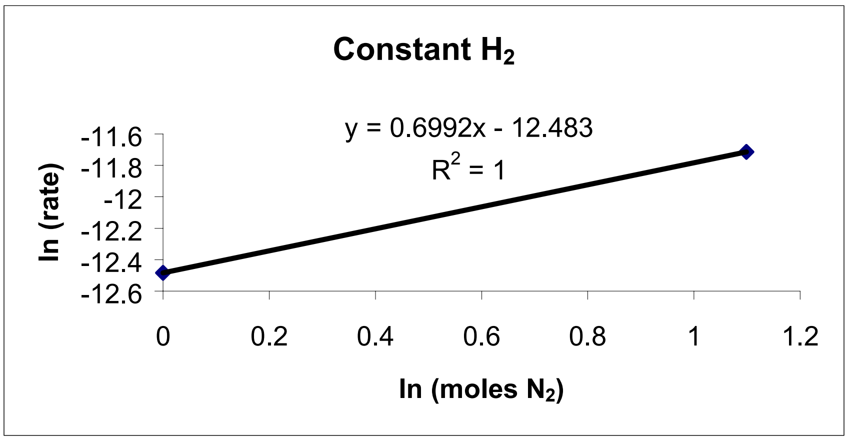
Write the Goldberg-Waage form of the rate equation and take the natural log of both sides.

$$\text{rate} = \frac{d\xi}{dt} = k[N_2]^{\alpha}[H_2]^{\beta} \tag{6}$$

$$\ln(\text{rate}) = \ln(k) + \alpha \ln[N_2] + \beta \ln[H_2] \tag{7}$$

To find α plot ln(rate) vs. $\ln[N_2]$ at a constant $[H_2]$, where $\ln[N_2] = \ln[\text{moles of } N_2]$.

rate	**moles N_2**	**moles H_2**
8.17×10^{-6}	3	1
3.79×10^{-6}	1	1
2.40×10^{-6}	1	3



From the graph, α = slope. Similarly, find β by plotting ln(rate) vs. $\ln[H_2]$ while holding $[N_2]$ constant.

$\alpha = 0.70$
$\beta = -0.42$

Therefore, the final rate expression is $\text{rate} = k[N_2]^{0.70}[H_2]^{-0.42}$. Finally, find the rates of ammonia synthesis for each ratio.

$$\frac{dn_{NH_3}}{dt} = 2\frac{d\xi}{dt} \tag{8}$$

Therefore,

N_2:H_2:He	$\frac{dn_{NH_3}}{dt}\left(\frac{\text{mol}}{\text{gcat}\cdot\text{min}}\right)$
3:1:0	8.17 x 10^{-5}
1:1:2	3.79 x 10^{-5}
1:3:0	2.40 x 10^{-5}

Exercise 11:

In Example 1.5.6 the following equations for t_{max} and C_B are derived.

$$t_{\max} = \frac{1}{k_2 - k_1} \cdot \ln\left[\frac{k_2}{k_1} + \frac{k_2}{k_1}\frac{C_B^o}{C_A^o} - \left(\frac{k_2}{k_1}\right)^2 \frac{C_B^o}{C_A^o}\right] \tag{1}$$

$$C_B = C_B^o \cdot e^{(-k_2 t)} + \frac{k_1 C_A^o}{k_2 - k_1}\left[e^{(-k_1 t)} - e^{(-k_2 t)}\right] \tag{2}$$

Assuming $C_B^o = 0$ and $k_2 = k_1$, C_B and $t_{\max} = \frac{0}{0}$. Therefore, use L'Hopital's rule to find t_{max} and C_B.

$$\lim_{k_2 \to k_1} t_{\max} = \lim_{k_2 \to k_1} \frac{1/k_1}{k_2/k_1} = \frac{1}{k_1} \tag{3}$$

$$\lim_{k_2 \to k_1} C_B = \lim_{k_2 \to k_1} k_1 C_A^o t_{\max} \cdot e^{(-k_2 t_{\max})} \tag{4}$$

Substituting for t_{max} gives:

$$C_B^{\max} = \frac{C_A^o}{e} \tag{5}$$

Exercise 12:

Part a)

Assign rate constants, k_i, to equations 1,2, and 3.

$$R + G \xrightarrow{k_1} 2R \tag{1}$$
$$L + R \xrightarrow{k_2} 2L \tag{2}$$

$$L \xrightarrow{k_3} D \quad (3)$$

Derive rate equations for each equation.

$$\mathrm{r}_1 = k_1 C_R C_G \quad (4)$$
$$\mathrm{r}_2 = k_2 C_L C_R \quad (5)$$
$$\mathrm{r}_3 = k_3 C_L \quad (6)$$

Express the accumulation rate of each species in terms of the above rates.

$$\frac{dC_R}{dt} = 2\mathrm{r}_1 - \mathrm{r}_1 - \mathrm{r}_2 \quad (7)$$
$$\frac{dC_L}{dt} = 2\mathrm{r}_2 - \mathrm{r}_2 - \mathrm{r}_3 \quad (8)$$

Substituting equations (4), (5), and (6) gives:

$$\frac{dC_R}{dt} = k_1 C_R C_G - k_2 C_L C_R \quad (9)$$
$$\frac{dC_L}{dt} = k_2 C_L C_R - k_3 C_L \quad (10)$$

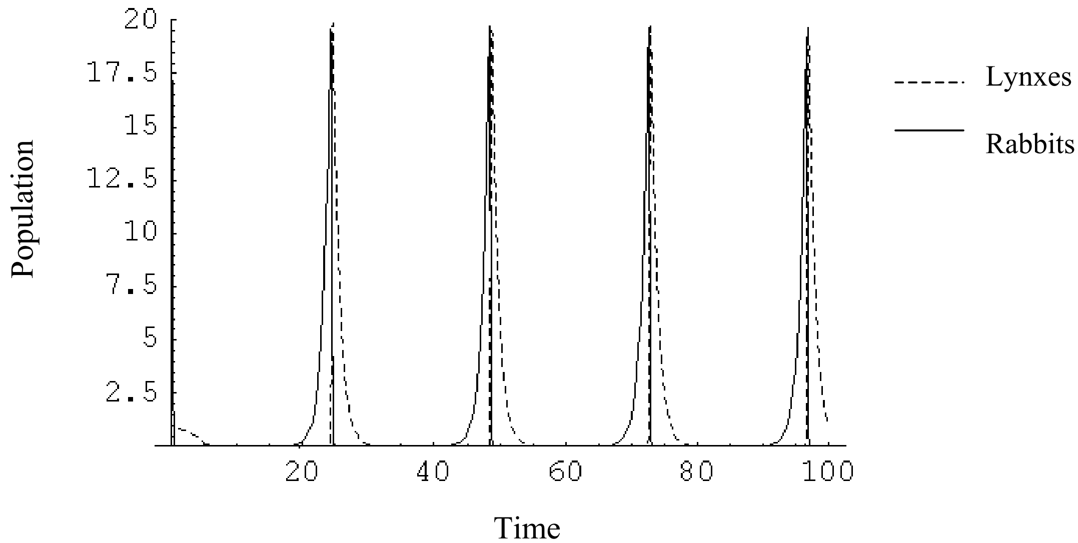
Part b)

Solve differential equations using most convenient solver.

$$\frac{dC_R}{dt} = C_R - C_R C_L \qquad \frac{dC_L}{dt} = C_R C_L - C_L$$

With initial conditions

$$C_R(0) = 20 \qquad C_L(0) = 1$$



Exercise 13:

Write the rate expression for DEBA, assuming constant volume.

$$\text{r} = \frac{dC_{DEBA}}{dt} = kC_{DEA}C_{BB} \tag{1}$$

Find C_{DEA} and C_{BB} in terms of C_{DEBA}.

$$C_{DEA} = C^o_{DEA} + \left(\frac{-1}{1}\right)(C_{DEBA} - C^o_{DEBA}) \tag{2}$$

$$C_{BB} = C^o_{BB} + \left(\frac{-1}{1}\right)(C_{DEBA} - C^o_{DEBA}) \tag{3}$$

Substitute equations (2) and (3) into equation (1), using the initial conditions given for 1,4-butanediol and acetonitrile, respectively.

$$\frac{dC_{DEBA}}{dt} = k(0.5 - C_{DEBA})(0.5 - C_{DEBA}) \tag{4}$$

$$\frac{dC_{DEBA}}{dt} = k(1 - C_{DEBA})(0.1 - C_{DEBA}) \tag{5}$$

Rearrange equations (4) and (5), and integrate to find C_{DEBA} as a function of time for each solvent.

1,4-butanediol:

$$\int_0^{C_{DEBA}} \frac{dC_{DEBA}}{(0.5 - C_{DEBA})^2} = \int_0^t k \cdot dt \tag{6}$$

$$\frac{1}{(0.5 - C_{DEBA})} = kt + 2 \tag{7}$$

acetonitrile:

$$\int_0^{C_{DEBA}} \frac{dC_{DEBA}}{(1 - C_{DEBA})(0.1 - C_{DEBA})} = \int_0^t k \cdot dt \tag{8}$$

$$\ln\left(\frac{1 - C_{DEBA}}{1 - 10C_{DEBA}}\right) = \frac{9}{10} kt \tag{9}$$

Using equations (7) and (9), find the rate constant (*k*) for each solvent.

1,4-butanediol: $k = 0.000212$ L mol^{-1} min^{-1}

acetonitrile $k = 0.00160$ L mol^{-1} min^{-1}

Exercise 14:

Write the first order rate equation for variable volume, Equation 1.5.3,

$$\frac{dn_A}{dt} = -kn_A \tag{1}$$

Rearrange and integrate equation (1) to find $\frac{n_A}{n_A^o}$.

$$\int_{n_A^o}^{n_A} \frac{dn_A}{n_A} = \int_0^t k \cdot dt \tag{2}$$

$$\frac{n_A}{n_A^o} = e^{(-kt)} \tag{3}$$

Use the ideal gas law to derive an expression for $\frac{n_{total}}{n_{total}^{o}}$.

$$\frac{P_{tot}V}{P_{tot}V^{o}} = \frac{n_{tot}RT}{n_{tot}^{o}RT} \tag{4}$$

$$\frac{n_{tot}}{n_{tot}^{o}} = \frac{V}{V^{o}} = \frac{.7V^{o} + V^{o}}{V^{o}} = 1.7 \tag{5}$$

Define the molar expansion factor and find $\frac{n_A}{n_A^{o}}$.

$$\varepsilon_A = 1 \cdot \left(\frac{3-1}{|-1|} \right) = 2 \tag{6}$$

$$\frac{n_{tot}}{n_{tot}^{o}} = 1 + 2f_A = 1.7 \qquad \text{Where } f_A = 1 - \frac{n_A}{n_A^{o}} \tag{7}$$

$$\frac{n_A}{n_A^{o}} = 0.65 \tag{8}$$

Solving for k in equation (3) gives $k = 0.000598\ \text{sec}^{-1}$.

To find the time needed to raise the pressure from 1.8 atm to 2.5 atm, first find $\frac{n_{total}}{n_{total}^{o}}$.

$$\frac{n_{tot}}{n_{tot}^{o}} = \frac{P}{P^{o}} = \frac{2.5}{1.8} = 1.389 \tag{9}$$

Using the value from equation (9), find $\frac{n_A}{n_A^{o}}$.

$$\frac{n_{tot}}{n_{tot}^{o}} = 1 + \varepsilon_A f_A = 1.389 \tag{10}$$

$$\frac{n_A}{n_A^{o}} = 0.8055 \tag{11}$$

Solving for time (t) in equation (3) gives $t = 361.7$ s.

Exercise 15:

For the constant volume reactor, express equilibrium constant (K) in terms of concentrations.

$$K = \frac{k_1}{k_2} = \frac{C_C}{C_A C_B} \tag{1}$$

Write the mole balance for the reaction.

	Initial	Change	Equilibrium
A	1	-ξ	1 – ξ
B	2	-ξ	2 – ξ
C	0	ξ	ξ
Total	3	-ξ	3 – ξ

Rewrite equation (1) in terms of ξ and pressure.

$$K = 2\ Lmol^{-1} = \frac{(\xi)}{(1-\xi)(2-\xi)} \tag{2}$$

Solving for ξ, gives ξ = 0.719 mol L^{-1}.

Using the ideal gas law, find P_{tot}^{eq} in terms of ξ.

$$P_{tot}^{eq} V = n_{tot}^{eq} RT \tag{3}$$

$$P_{tot}^{eq} = \frac{n_{tot}^{eq} RT}{V} = (3-\xi)RT \tag{4}$$

Therefore,

Fractional conversion of A (f_A) = 0.719
Final pressure (P_{tot}^{eq}) = 56.2 atm

Write rate equation for species A.

$$rate = -\frac{dC_A}{dt} = k_1 C_A C_B - k_2 C_C \tag{5}$$

Express all concentrations in terms of C_A.

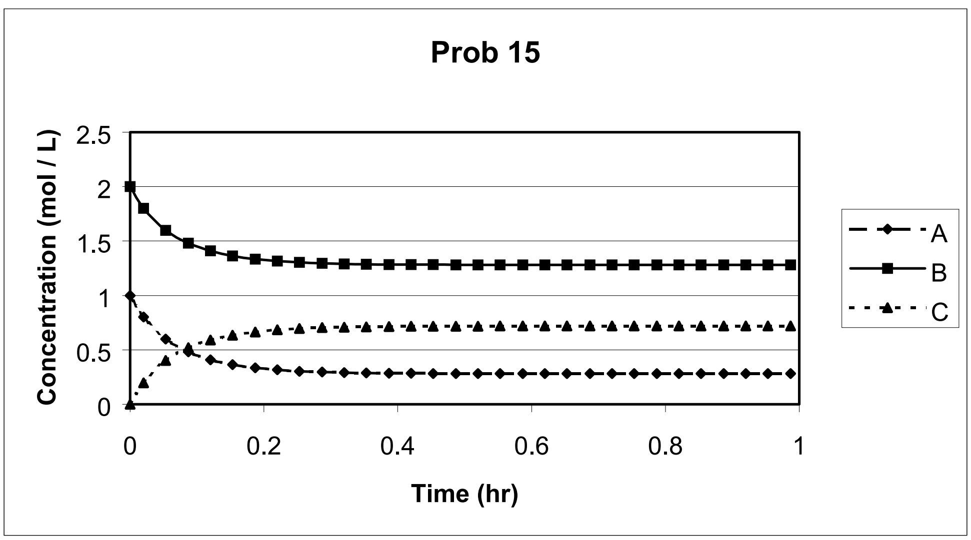
$$C_B = C_B^o + \left(\frac{-1}{-1}\right)(C_A - C_A^o) \tag{6}$$

$$C_C = C_C^o + \left(\frac{-1}{1}\right)(C_A - C_A^o) \tag{7}$$

Substitute equations (6) and (7) into equation (5).

$$rate = -\frac{dC_A}{dt} = k_1 C_A (1 + C_A) - k_2 (1 - C_A) \tag{8}$$

Solve by hand or with a computer solver for each species and plot the composition of the reactor versus time.



Exercise 16:

For the variable volume reactor, express equilibrium constant (K) in terms of mole fractions and total pressure.

$$K = \frac{k_1}{k_2} = \frac{X_C}{X_A X_B} \cdot \frac{1}{P_{tot}} \tag{1}$$

Using the mole balance from Exercise 15, express equation (1) in terms of ξ and P_{tot}.

$$K = 2\,\tfrac{\text{L}}{\text{mol}} = \frac{\left(\dfrac{\xi}{3-\xi}\right)}{\left(\dfrac{1-\xi}{3-\xi}\right)\left(\dfrac{2-\xi}{3-\xi}\right)\cdot P_{tot}} \tag{2}$$

Using the ideal gas law, the equilibrium constant can be rewritten as 0.08124 atm^{-1}.

Again, use the ideal gas law to find P_{tot} and solve for ξ.

$$P_{tot} = \frac{n_{tot}^{o} RT}{V^{o}} = 73.85\,\text{atm} \tag{3}$$

$$\xi = 0.7681 \tag{4}$$

Therefore, the equilibrium conversion of A = 0.7681.

Write the rate equation for species A.

$$rate = -\frac{1}{V}\frac{dn_A}{dt} = k_1 C_A C_B - k_2 C_C \tag{5}$$

$$rate = -\frac{dn_A}{dt} = \frac{k_1 n_A n_B}{V} - k_2 n_C \tag{6}$$

Express V in terms of V^o and n_A.

$$V = V^{o}(1 + \varepsilon_A f_A) \tag{7}$$

$$\varepsilon_A = \frac{1}{3}\left[\frac{-1}{|-1|}\right] = -\frac{1}{3} \quad \text{And} \quad f_A = 1 - \frac{n_A}{n_A^{o}} \tag{8}$$

Therefore, $V = V^{o}\left(\dfrac{2}{3} + \dfrac{1}{3} n_A\right)$ (9)

Express n_B and n_C in terms of n_A.

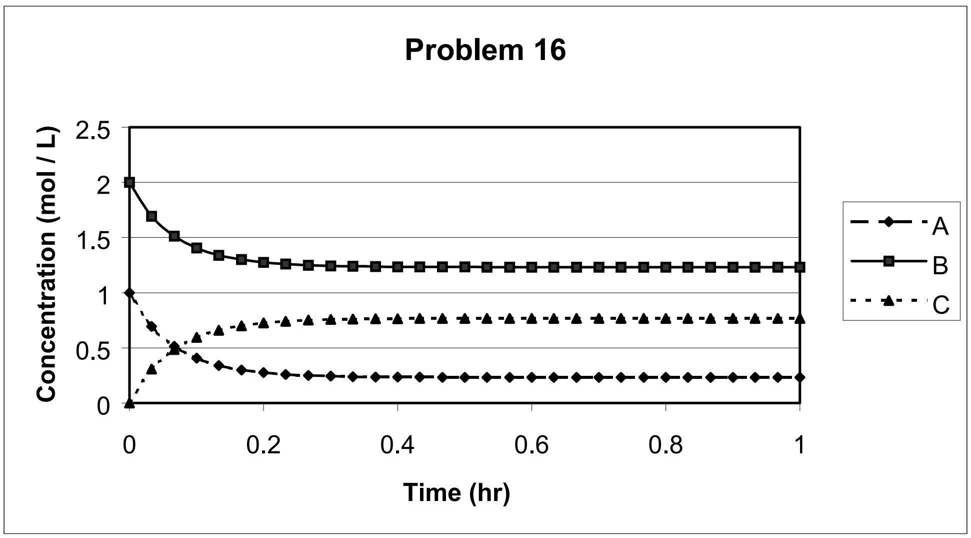
$$n_B = n_B^{o} + \left(\frac{-1}{-1}\right)(n_A - n_A^{o}) = 1 + n_A \tag{10}$$

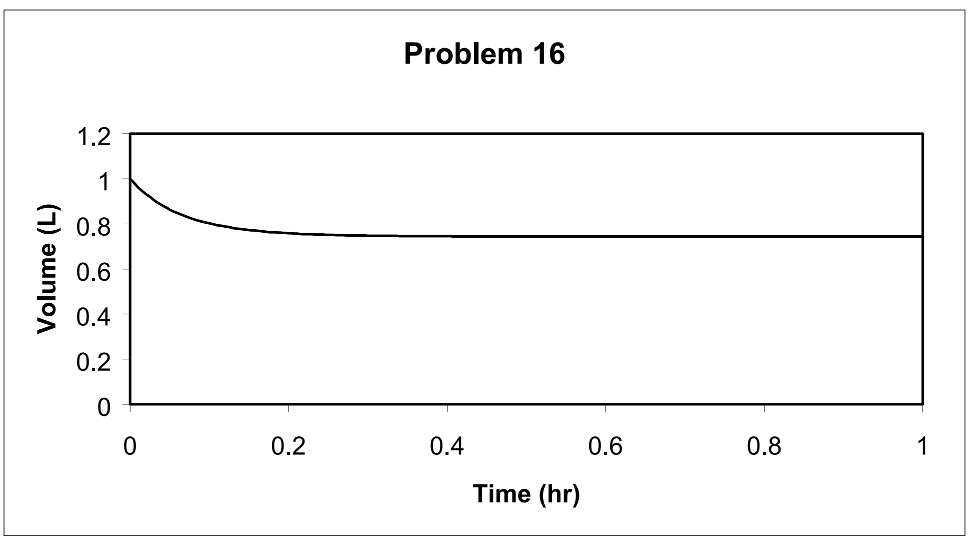
$$n_C = n_C^o + \left(\frac{-1}{1}\right)(n_A - n_A^o) = 1 - n_A \qquad (11)$$

Substitute equations (9), (10), and (11) into equation (6).

$$-\frac{dn_A}{dt} = -\frac{dn_B}{dt} = \frac{dn_C}{dt} = \frac{3k_1 n_A (1+n_A)}{V^o (2+n_A)} - k_2 (1-n_A) \qquad (12)$$

Solve for each species by hand or with a computer solver and plot the composition of the reactor and the volume versus time.





Exercise 17:

Write a new mole balance to account for the inert gas.

	Initial	Change	Equilibrium
A	1	-ξ	$1-\xi$
B	2	-ξ	$2-\xi$
C	0	ξ	ξ
Inert	3	0	3
Total	6	-ξ	$6-\xi$

Solve for ξ, using a modified form of equation (2) from Exercise 16.

$$K = 0.08124\ \text{atm}^{-1} = \frac{\left(\dfrac{\xi}{6-\xi}\right)}{\left(\dfrac{1-\xi}{6-\xi}\right)\left(\dfrac{2-\xi}{6-\xi}\right)\cdot P_{tot}} \tag{1}$$

Use the ideal gas law to find P_{tot} and solve for ξ.

$$P_{tot} = \frac{n_{tot}^{o} RT}{V^{o}} = 147.7\ \text{atm} \tag{2}$$

$$\xi = 0.7417 \tag{3}$$

Therefore, the equilibrium conversion of A = 0.7417.

Write the rate equation for species A as done in Exercise 16.

$$rate = -\frac{dn_A}{dt} = \frac{k_1 n_A n_B}{V} - k_2 n_C \tag{4}$$

Express V in terms of V^o and n_A.

$$V = V^{o}(1 + \varepsilon_A f_A) \tag{5}$$

$$\varepsilon_A = \frac{1}{6}\left[\frac{-1}{|-1|}\right] = -\frac{1}{6} \quad \text{And} \quad f_A = 1 - \frac{n_A}{n_A^{o}} \tag{6}$$

Therefore, $V = V^{o}\left(\frac{5}{6} + \frac{1}{6} n_A\right)$ (7)

Express n_B and n_C in terms of n_A.

$$n_B = n_B^o + \left(\frac{-1}{-1}\right)(n_A - n_A^o) = 1 + n_A \quad (8)$$

$$n_C = n_C^o + \left(\frac{-1}{1}\right)(n_A - n_A^o) = 1 - n_A \quad (9)$$

Substitute equations (7), (8), and (9) into equation (4).

$$-\frac{dn_A}{dt} = -\frac{dn_B}{dt} = \frac{dn_C}{dt} = \frac{6k_1 n_A (1 + n_A)}{V^o (5 + n_A)} - k_2 (1 - n_A) \quad (10)$$

Solve for each species by hand or with a computer solver and plot the composition of the reactor and the volume versus time.