Solutions to workshop 03: Rate law and stoichiometry

Lecture notes for chemical reaction engineering

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Try following problems from Fogler 5e(Fogler 2016).

P3-5, P3-10, P3-11, P3-12, P 4-6, P 4-8, P 4-11

We will go through some of these problems in the workshop.

P 3.12

Write the rate law for the following reactions assuming each reaction follows an elementary rate law. Give the units of k_A for each, keeping in mind some are homogeneous and some reactants are heterogeneous.

1. $C_2H_6 \longrightarrow C_2H_4\,H_2$
2. $C_2H_4 + \frac{1}{2}O_2 \longrightarrow C_2H_4O$
3. $(CH_3)_3COOC(CH_3)_3 \rightleftharpoons C_2H_6 + 2\,CH_3COCH_3$
4. $nC_4H_{10} \rightleftharpoons iC_4H_{10}$
5. $CH_3COOC_2H_5 + C_4H_9OH \rightleftharpoons CH_3COOC_4H_9 + C_2H_5OH$
6. $2\,CH_3NH_2 \underset{cat}{\rightleftharpoons} (CH_3)_2NH + NH_3$
7. $(CH_3CO)_2O + H_2O \rightleftharpoons 2\,CH_3COOH$

> 💡 Solution
>
> 1. $-r_A = kC_A$
>
> 2. $-r_A = kC_A C_B^{1/2}$
>
> 3. $-r_A = k\left(C_A - \frac{C_B C_C}{K}\right)$
>
> 4. $-r_A = k\left(C_A - \frac{C_B}{K}\right)$
>
> 5. $-r_A = k\left(C_A C_B - \frac{C_C C_D}{K}\right)$

6. $-r'_A = k \left(P_A^2 - \frac{P_B P_C}{K} \right)$

7. $-r_A = k \left(C_A C_B - \frac{C_C^2}{K} \right)$

P3-10

The initial reaction rate for the elementary reaction $2\,A + B \longrightarrow 4\,C$ was measured as a function of temperature when the concentration of A was 2 M and that of B was 1.5 M.

$-r_A(mol/dm^3 s)$	$T(K)$
0.002	300
0.046	320
0.72	340
8.33	360

1. What is the activation energy?

2. What is the frequency factor?

3. What is the rate constant as a function of temperature using Equation 1 and T_0 = 27 °C as the base case?

$$k(T) = k(T_0)exp\left[\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T} \right) \right] \tag{1}$$

> 💡 Solution
>
> $2\,A + B \longrightarrow 4\,C$. Elementary reaction. Initial rates given.
> For elementary reaction
> $-r_A = kC_A^2 C_B$
> $k = \frac{-r_A}{C_A^2 C_B}$
> At the start of reaction:
> $k = \frac{-r_{A0}}{C_{A0}^2 C_{B0}}$

```python
import numpy as np
import matplotlib.pyplot as plt
from scipy.stats import linregress

# Data
r_A = np.array([0.002, 0.046, 0.72, 8.33])
T = np.array([300, 320, 340, 360])

R = 8.314 # J/mol K
C_A0 = 2.0
C_B0 = 1.5

k = r_A/(C_A0**2 * C_B0)

ln_k = np.log(k)
inv_T = 1 / T

slope, intercept, r_value, p_value, std_err = linregress(inv_T, ln_k)
line = slope * inv_T + intercept

activation_energy = -slope*R/1000 # (kJ/mol)
A0 = np.exp(intercept)

# Plot
plt.scatter(inv_T, ln_k, color='blue', label='Data points')
plt.plot(inv_T, line, color='red', label='Fit line')

# Labels and title
plt.xlabel('1/T (1/K)')
plt.ylabel('ln(k)')
plt.title('Linear Fit of ln(k) vs 1/T')
plt.legend()

slope_text = f'Slope: {slope:.2f}'
intercept_text = f'Intercept: {intercept:.2f}'
e_text = f'Activation Energy: {activation_energy:.2f} kJ/mol'
a0_text = f'Frequency factor: {A0:.2e} $dm^6/mol^2 s$'
plt.annotate(f'{slope_text}\n{intercept_text}\n{e_text}\n{a0_text}', xy=(0.05, 0.25),

# Show plot
plt.show()
```
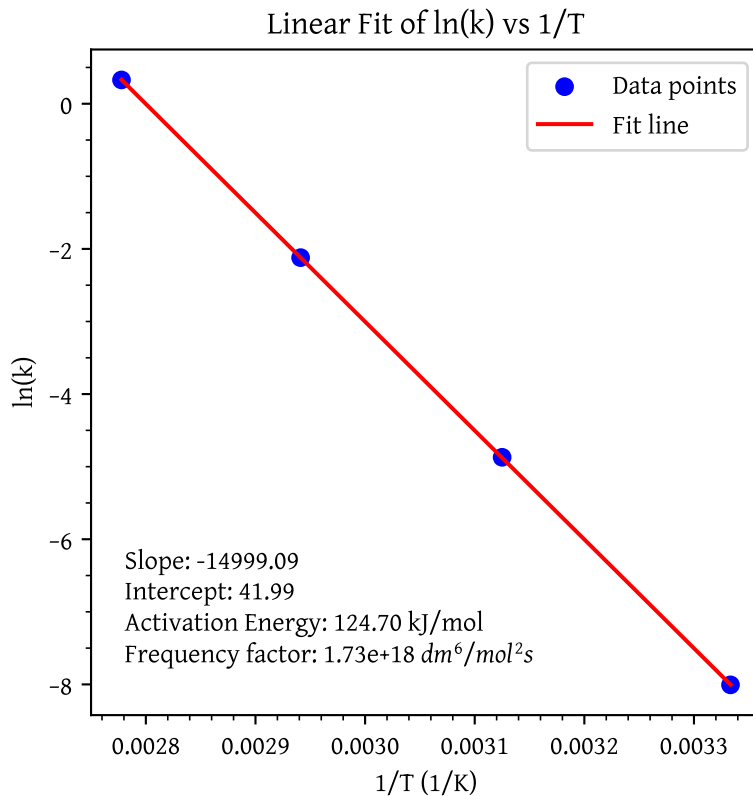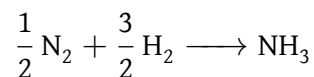
Linear Fit of ln(k) vs 1/T

Slope: -14999.09
Intercept: 41.99
Activation Energy: 124.70 kJ/mol
Frequency factor: 1.73e+18 dm^6/mol^2s

$$k = 1.73 \times 10^{18} \exp\left[\frac{-15000}{T}\right]$$

P 4-8

The gas-phase reaction

$$\frac{1}{2}\,N_2 + \frac{3}{2}\,H_2 \longrightarrow NH_3$$

is to be carried out isothermally first in a flow reactor. The molar feed is 50% H_2 and 50% N_2, at a pressure of 16.4 atm and at a temperature of $227\,^\circ C$?.

(a) Construct a complete stoichiometric table.

(b) Express the concentrations in mol/dm^3 of each for the reacting species as a function of conversion. Evaluate C_{A0}, δ and ϵ, and then calculate the concentrations of ammonia and hydrogen when the conversion of H_2 is 60%.

(c) Suppose by chance the reaction is elementary with $k_{N_2} = 40\,dm^3/mol/s$. Write the rate of reaction solely as a function of conversion for

    (1) a flow reactor, and for

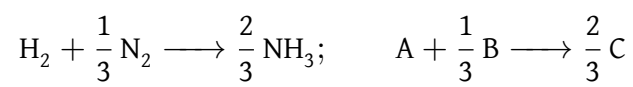   (2) a constant-volume batch reactor.

Solution

Gas phase reaction

$$\frac{1}{2}\,N_2 + \frac{3}{2}\,H_2 \longrightarrow NH_3$$
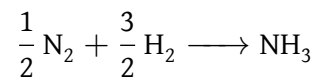
$y_A = 0.5$
$y_B = 0.5$
$P = 16.4\,atm$
$T = 227°C = 500K$

a. stoichiometric table

Basis of reaction: H_2

$$H_2 + \frac{1}{3}\,N_2 \longrightarrow \frac{2}{3}\,NH_3; \qquad A + \frac{1}{3}\,B \longrightarrow \frac{2}{3}\,C$$

Species	Entering	Change	Exiting
A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
B	$F_{B0} = \Theta_B F_{A0}$	$-F_{A0}X/3$	$F_A = F_{A0}(\Theta_B - X/3)$
C	0	$+(2/3)F_{A0}X$	$F_C = (2/3)F_{A0}X$

$\Theta_B = 1$

b. Conc. in mol/dm^3 as $f(X)$

$$\delta = c/a - b/a - 1 = 2/3 - 1/3 - 1 = -2/3$$

$$\epsilon = y_{A0}\delta = 0.5\delta = -1/3$$

$$C_{A0} = 0.2$$

$$C_A = \frac{C_{A0}(1-X)}{(1+\epsilon X)} \cdots \text{Constant P and T}$$

$$C_A = \frac{C_{A0}(1-X)}{(1+X/3)} \rightarrow X = 0.6 \rightarrow C_A = \frac{0.2(1-0.6)}{(1+0.6/3)} = 0.1 mol/dm^3$$

$$C_C = \frac{2}{3}\frac{C_{A0}(X)}{(1+\epsilon X)} \rightarrow X = 0.6 \rightarrow C_C = \frac{2}{3}\frac{0.2 \times 0.6}{(1+0.6/3)} = 0.1 mol/dm^3$$

c. $-r_A$ as $f(X)$, $k_{N_2} = 40 dm^3/mols$

1. Flow reactor

$$-r_{N_2} = k_{N_2}C_{N_2}^{1/2}C_{H_2}^{3/2}$$

$$-r_{N_2} = 40\left[\frac{C_{A0}(\Theta_B - X/3)}{(1+\epsilon X)}\right]^{1/2}\left[\frac{C_{A0}(1-X)}{(1+\epsilon X)}\right]^{3/2}$$

$$-r_{N_2} = 40C_{A0}^2\left[\frac{(1-X)}{(1-X/3)}\right]^{3/2} = 1.6\left[\frac{(1-X)}{(1-X/3)}\right]^{3/2}$$
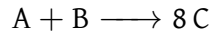
2. For constant volume batch reactor

$$-r_{N_2} = k_{N_2}C_{N_2}^{1/2}C_{H_2}^{3/2}$$

$$-r_{N_2} = 40C_{A0}^2(1-X/3)^{1/2}(1-X)^{3/2} = 1.6(1-X/3)^{1/2}(1-X)^{3/2}$$

P 4-11

Consider a cylindrical batch reactor that has one end fitted with a frictionless piston attached to a spring (See Figure Figure 1). The reaction

$$A + B \longrightarrow 8\,C$$

with the rate law

$$-r_A = k_1 C_A^2 C_B$$
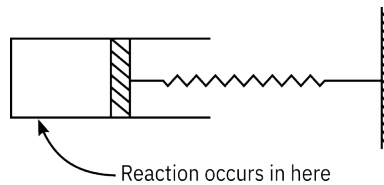
is taking place in this type of reactor.

Figure 1: Cylindrical batch reactor

(a) Write the rate law solely as a function of conversion, numerically evaluating all possible symbols.

(b) What is the conversion and rate of reaction when $V = 0.2 \; ft^3$?

Additional information:

Equal moles of A and B are present at t_0

Initial volume: $0.15 \; ft^3$

Value of k_1 : $1.0 \; (ft^3/lbmol)^2 \cdot s^{-1}$

The spring constant is such that the relationship between the volume of the reactor and pressure within the reactor is

$V = (0.1)\,(P)$ (V in ft^3 , P in atm)

Temperature of system (considered constant): $140\,^\circ F$

Gas constant: $0.73 \; ft^3 atm/lbmol \cdot^\circ R$

> **Solution**
>
> a. Rate law as f(X)
>
> $$y_{A0} = \frac{N_{A0}}{N_{A0} + N_{B0}} = 0.5$$
>
> $$\delta = 8 - 1 - 1 = 6$$
>
> $$\epsilon = y_{A0}\delta = 3$$
>
> $$V = V_0(1 + \epsilon X)\frac{P_0}{P}\frac{T}{T_0}$$

$$P_0 = 10V_0; \quad P = 10V$$

$$V = \frac{10V_0^2}{10V}(1 + \epsilon X)$$

$$V^2 = V_0^2(1 + \epsilon X)$$

$$N_A = N_{A0}(1 - X); \quad N_B = N_{A0}(\Theta_B - X)$$

$$\Theta_B = \frac{N_{B0}}{N_{A0}} = 1$$

$$-r_A = kC_A^2 C_B = \frac{kN_A^2 N_B}{V^2} = \frac{kN_{A0}^3(1 - X)^3}{V_0^3(1 + \epsilon X)^3/2}$$

$$\frac{N_{A0}}{V_0} = \frac{y_{A0}P}{RT}$$

$$\therefore -r_A = k\left(\frac{y_{A0}P_0}{RT}\right)^3 \left(\frac{(1 - X)}{(1 + \epsilon X)^{1/2}}\right)^3$$

$$-r_A = 5.02 \times 10^{-9} \left(\frac{(1 - X)}{(1 + \epsilon X)^{1/2}}\right)^3$$

b. X and $-r_A$ at $V = 0.2 ft^3$

$$V^2 = V_0^2(1 + \epsilon X)$$

$$(0.2)^2 = (0.15)^2(1 + 3X) \Rightarrow X = 0.259$$

$$-r_A = 8.623 \times 10^{-10} lbmol/ft^3 s$$

Fogler, H. Scott. 2016. *Elements of Chemical Reaction Engineering.* Fifth edition. Boston: Prentice Hall.