

# Solutions to workshop 03: Rate law and stoichiometry

Lecture notes for chemical reaction engineering

Ranjeet Utikar

2024-03-10

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.

- $C_2H_6 \longrightarrow C_2H_4 + H_2$
- $C_2H_4 + \frac{1}{2} O_2 \longrightarrow C_2H_4O$
- $(CH_3)_3COOC(CH_3)_3 \rightleftharpoons C_2H_6 + 2 CH_3COCH_3$
- $nC_4H_{10} \rightleftharpoons iC_4H_{10}$
- $CH_3COOC_2H_5 + C_4H_9OH \rightleftharpoons CH_3COOC_4H_9 + C_2H_5OH$
- $2 CH_3NH_2 \xrightleftharpoons{cat} (CH_3)_2NH + NH_3$
- $(CH_3CO)_2O + H_2O \rightleftharpoons 2 CH_3COOH$

### Solution

- $-r_A = kC_A$
- $-r_A = kC_A C_B^{1/2}$
- $-r_A = k \left( C_A - \frac{C_B C_C}{K} \right)$
- $-r_A = k \left( C_A - \frac{C_B}{K} \right)$
- $-r_A = k \left( C_A C_B - \frac{C_C C_D}{K} \right)$

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

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

### P3-10

The initial reaction rate for the elementary reaction  $2A + B \longrightarrow 4C$  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 <sup>3</sup> 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  $T_0 = 27^\circ\text{C}$  as the base case?

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

#### Solution

$2A + B \longrightarrow 4C$ . Elementary reaction. Initial rates given.

For elementary reaction

$$-r_A = k C_A^2 C_B$$

$$k = \frac{-r_A}{C_A^2 C_B}$$

At the start of reaction:

$$k = \frac{-r_{A0}}{C_{A0}^2 C_{B0}}$$

```

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)

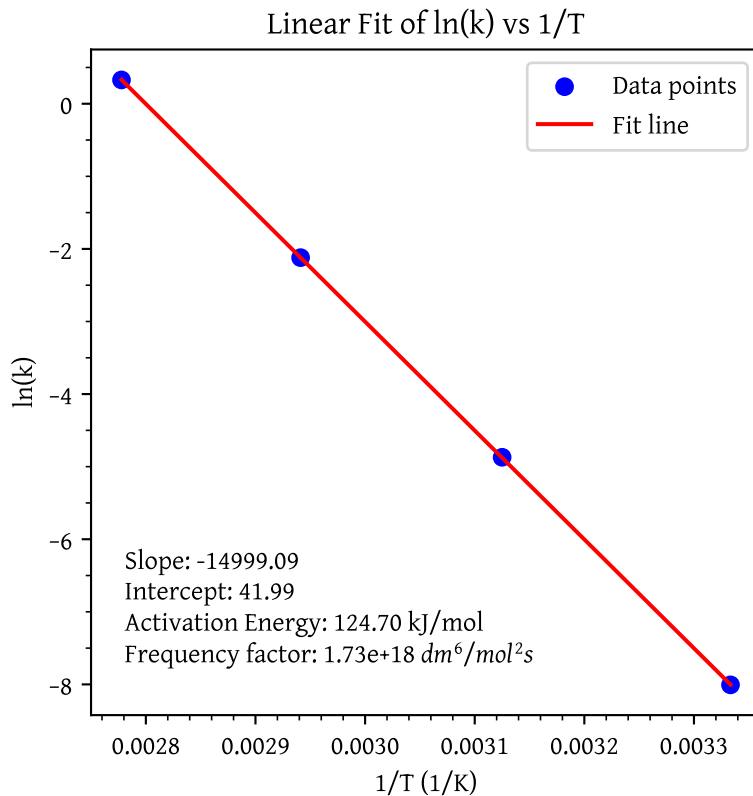
# Plot
plt.scatter(inv_T, ln_k, color='blue', label='Data points')
plt.plot(inv_T, line, color='red', label='Fit line')

# 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()

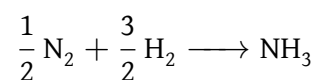
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$$k = 1.73 \times 10^{18} \exp \left[ \frac{-15000}{T} \right]$$

## P 4-8

The gas-phase reaction

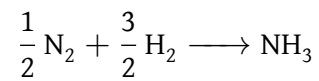


is to be carried out isothermally first in a flow reactor. The molar feed is 50%  $\text{H}_2$  and 50%  $\text{N}_2$ , at a pressure of 16.4 atm and at a temperature of  $227^\circ\text{C}$ .

- (a) Construct a complete stoichiometric table.
- (b) Express the concentrations in  $\text{mol}/\text{dm}^3$  of each for the reacting species as a function of conversion. Evaluate  $C_{A0}$ ,  $\delta$  and  $\epsilon$ , and then calculate the concentrations of ammonia and hydrogen when the conversion of  $\text{H}_2$  is 60%.
- (c) Suppose by chance the reaction is elementary with  $k_{\text{N}_2} = 40 \text{ dm}^3/\text{mol}/\text{s}$ . 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



$$y_A = 0.5$$

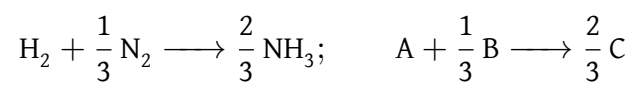
$$y_B = 0.5$$

$$P = 16.4 \text{ atm}$$

$$T = 227^\circ \text{C} = 500 \text{ K}$$

a. stoichiometric table

Basis of reaction:  $\text{H}_2$



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  $f(X)$

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

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

$$C_{A0} = 0.2$$

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

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

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

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

1. Flow reactor

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

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

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

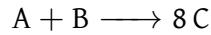
2. For constant volume batch reactor

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

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

## 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



with the rate law

$$-r_A = k_1 C_A^2 C_B$$

is taking place in this type of reactor.

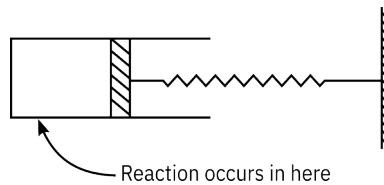


Figure 1: Cylindrical batch reactor

- Write the rate law solely as a function of conversion, numerically evaluating all possible symbols.
- What is the conversion and rate of reaction when  $V = 0.2 \text{ ft}^3$ ?

Additional information:

Equal moles of A and B are present at  $t_0$

Initial volume:  $0.15 \text{ ft}^3$

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

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

$$V = (0.1) (P) \quad (V \text{ in } \text{ft}^3, P \text{ in } \text{atm})$$

Temperature of system (considered constant):  $140^\circ \text{F}$

Gas constant:  $0.73 \text{ ft}^3 \text{ atm} / \text{lbmol} \cdot ^\circ \text{R}$

### 💡 Solution

a. Rate law as  $f(X)$

$$y_{A0} = \frac{N_{A0}}{N_{A0} + N_{B0}} = 0.5$$

$$\delta = 8 - 1 - 1 = 6$$

$$\epsilon = y_{A0} \delta = 3$$

$$V = V_0 (1 + \epsilon X) \frac{P_0}{P} \frac{T}{T_0}$$

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

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

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

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

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

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

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

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

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

b.  $X$  and  $-r_A$  at  $V = 0.2 \text{ ft}^3$

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

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

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

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