

## Assignment 2 Solutions

1. In a liquid phase reaction, 30% of the reactant disappears in 34 minutes for initial reactant concentrations of 0.04 and also for 0.8 mol/liter. What rate law represents the disappearance of the reactant? [2 Marks]

For zeroth order,  $C_A = C_{A0} - k_0 t$ ;  $X = \frac{k_0 t}{C_{A0}}$ ; conversion depends on initial reactant concentration. So it can not be a zeroth order reaction.

For first order,  $\ln\left(\frac{C_{A0}}{C_A}\right) = k_1 t$ ;  $\ln\left(\frac{1}{1-X}\right) = k_1 t$ ; conversion is independent of initial concentration. So the given data satisfies first order kinetics.

$$k_1 = \frac{1}{t} \ln\left(\frac{1}{1-X}\right) = 0.01 \text{ min}^{-1}.$$

Rate law:  $-r_A = 0.01 (\text{min}^{-1}) C_A$ .

2. In a batch reactor, a reactant, with  $C_{A0} = 1$  mol/liter, is converted 80% in 8 min; and after 18 min, the conversion is 90%. Find a rate law to represent this reaction. [2 Marks]

Data:  $X_1 = 0.8$ ,  $t_1 = 8$  min

$X_2 = 0.9$ ,  $t_2 = 18$  min

Clearly the order is not zero, because conversion does not increase with time proportionally.

The data does not fit first order kinetics either ( $k_1$  for the two conditions are not the same).

Test with 2<sup>nd</sup> order kinetics:

$$\left(\frac{X}{1-X}\right) \frac{1}{C_{A0} t} = k_2$$

The data given above satisfy 2<sup>nd</sup> order kinetics, with  $k_2 = 0.5 \text{ min}^{-1}$ .

Rate law:  $-r_A = 0.5 (\text{l}^3 \text{mol}^{-1} \text{min}^{-1}) C_A^2$ .

3. A first order reversible liquid-phase reaction  $A \leftrightarrow B$  takes place in a constant volume batch reactor. With  $C_{A0} = 0.5$  mol/liter and  $C_{B0} = 0$ , after 8 minutes conversion of A is 0.333 while equilibrium conversion is 0.667. Find the rate law for this reaction. [2 Marks]

Stoichiometry:  $C_A = C_{A0}(1 - X)$   
 $C_B = C_{A0}X$

Equilibrium constant:  $K = \frac{C_{Be}}{C_{Ae}} = \frac{C_{A0}X_e}{C_{A0}(1-X_e)} = 2$

Rate law:  $-r_A = k_1 C_A - k_2 C_B$

$$\frac{dX}{dt} = k_1 [1 - (1 + K^{-1})X]$$

Integration:  $\frac{1}{(1+K^{-1})t} \ln \left( \frac{1}{1-(1+K^{-1})X} \right) = k_1$

Substituting  $K = 2$ ,  $t = 8 \text{ min}$ ,  $X = 0.333$ ,  $k_1 = 0.0576 \text{ min}^{-1}$ ,  $k_2 = 0.0288 \text{ min}^{-1}$ .

$$-r_A = 0.0576 (\text{min}^{-1}) C_A - 0.0288 (\text{min}^{-1}) C_B$$

4. The kinetics of thermal decomposition of species A is carried out in a differential packed bed reactor. From the data given in the table below, determine the rate law parameters.

Run	Rate mol/(liter.s)	Concentration of A in the reactor mol/liter	Temperature (K)
1	$4.9 \times 10^{-4}$	0.2	700
2	$1.1 \times 10^{-4}$	0.02	750
3	$2.4 \times 10^{-3}$	0.05	800
4	$2.2 \times 10^{-2}$	0.08	850
5	$1.18 \times 10^{-1}$	0.1	900
6	$1.82 \times 10^{-2}$	0.06	950

*Hint:* Use Arrhenius equation [ $k = A \exp(-E_a/RT)$ ] for temperature dependence of rate constant. Use non-linear regression using MATLAB to obtain  $\alpha$ , A, and  $E_a$ . Include the MATLAB code in your solution. [4 Marks]

$$-r_A = A e^{-E/RT} C_A^\alpha$$

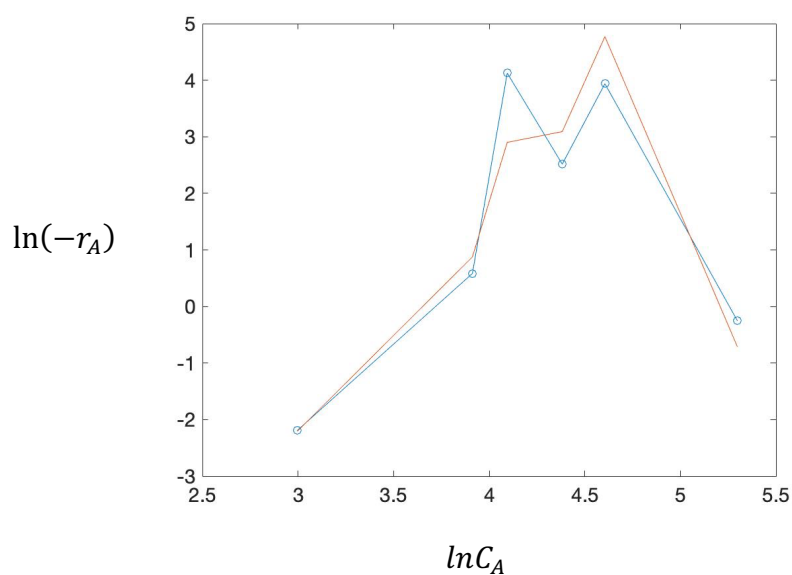
$$\ln(-r_A) = \ln A - \frac{E}{RT} + \alpha \ln C_A$$

Using non-linear regression using the above form of rate law:

$$\ln A = 15.2786; A = 4.3 \times 10^6 \left( \frac{\text{mol}}{\text{m}^3} \right)^{0.5} \frac{1}{\text{s}}$$

$$\alpha \approx 1.5$$

$$E = 1.37 \times 10^5 \text{ J/mol}$$



5. The following data are obtained at 0 °C in a constant volume batch reactor using pure gaseous A:

Time (min)	0	2	4	6	8	10	12	14	$\infty$
Partial pressure mmHg	760	600	475	390	320	275	240	215	150

The stoichiometry of the decomposition is  $A \rightarrow 2.5R$ . Find a rate law which satisfactorily represents this decomposition using (i) Integral approach and (ii) Differential approach.

At time tending to infinity,  $p_A$  is finite, indicating reversible reaction.

*Differential approach:* [5 Marks]

$$-\frac{dp_A}{dt} = k'_1 p_A - k'_2 p_B \quad [\text{Order is assumed to be 1.}]$$

$$p_A = p_{A0}(1 - X)$$

$$p_B = 2.5p_{A0}X$$

$$\text{At equilibrium: } K_P = \frac{p_{Be}}{p_{Ae}} = \frac{2.5 \times (p_{A0} - p_{Ae})}{p_{Ae}} = \frac{2.5 \times (760 - 150)}{150} = 10.17$$

$$-\frac{dp_A}{dt} = k'_1(p_A - K_P^{-1}p_B)$$

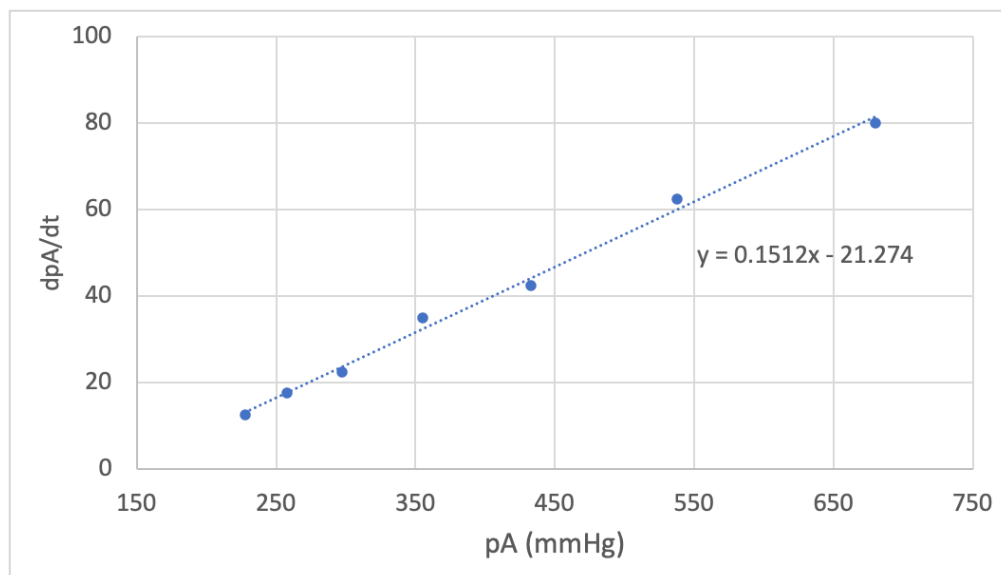
$$-\frac{dp_A}{dt} = k'_1[p_A - 2.5K_P^{-1}(p_{A0} - p_A)]$$

$$-\frac{dp_A}{dt} = k'_1[p_A(1 + 2.5K_P^{-1}) - 2.5K_P^{-1}p_{A0}]$$

Calculate  $-\frac{dp_A}{dt}$ :

Time (min)	0	2	4	6	8	10	12	14	$\infty$
Partial pressure mmHg	760	600	475	390	320	275	240	215	150
$p_{Am}$ (mid point)	-	680	537.5	432.5	355	297.5	257.5	227.5	-
$-\frac{dp_A}{dt}$	-	80	62.5	42.5	35	22.5	17.5	12.5	

Plot  $-\frac{dp_A}{dt}$  vs  $p_A$



$$-\frac{dp_A}{dt} = 0.1512p_A - 21.274$$

$$(1 + 2.5K_P^{-1})k'_1 = 0.1512$$

$k'_1 = 0.12 \text{ min}^{-1}$ ;  $k'_2 = 0.012 \text{ min}^{-1}$ .  $K_P$  calculated from the intercept (10.7) is very close to 10.17, based on equilibrium experimental data.

The rate law is given as:

$$-\frac{dp_A}{dt} = 0.12 (\text{min}^{-1})p_A - 0.012(\text{min}^{-1})p_B$$

Integral approach: [5 Marks]

$$-\frac{dp_A}{dt} = k'_1[p_A(1 + 2.5K_P^{-1}) - 2.5K_P^{-1}p_{A0}]$$

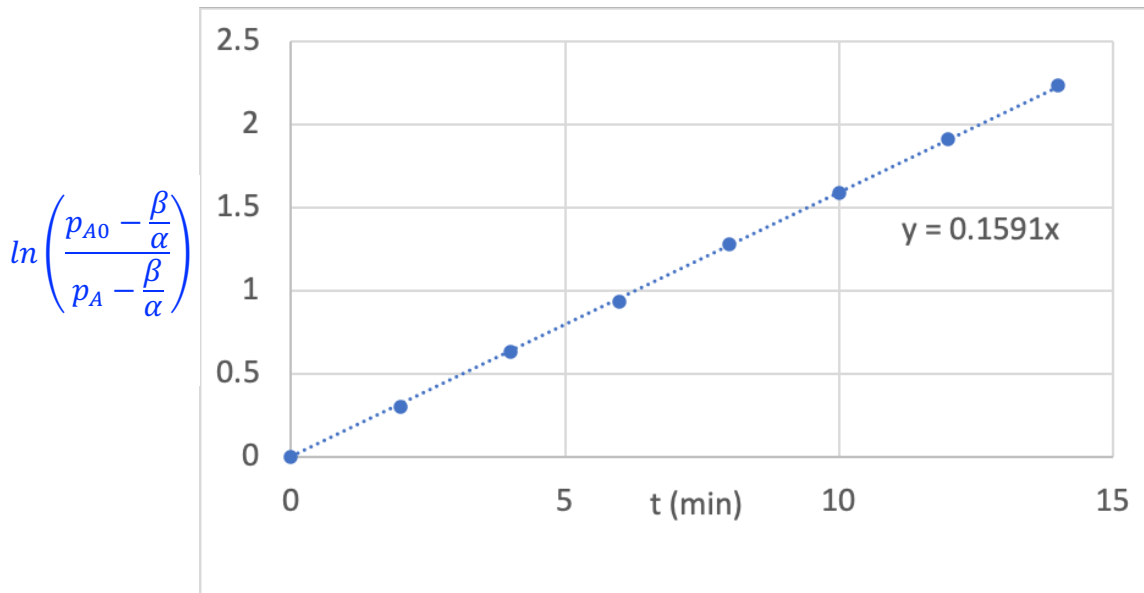
$$-\frac{dp_A}{dt} = \alpha p_A - \beta$$

Where  $\alpha = (1 + 2.5K_P^{-1})k'_1$ ;  $\beta = 2.5K_P^{-1}k'_1 p_{A0}$ ;  $\frac{\beta}{\alpha} = 150 \text{ mmHg}$

Note that  $\frac{\beta}{\alpha}$  is the equilibrium partial pressure of A.

Integrating the differential equation:

$$\ln \left( \frac{p_{A0} - \frac{\beta}{\alpha}}{p_A - \frac{\beta}{\alpha}} \right) = \alpha t$$



$$\alpha = (1 + 2.5K_P^{-1})k'_1 = 0.1591,$$

$$k'_1 = 0.128 \text{ min}^{-1}$$

$$k'_2 = 0.012 \text{ min}^{-1}$$

The rate law is given as:

$$-\frac{dp_A}{dt} = 0.128 (\text{min}^{-1})p_A - 0.012(\text{min}^{-1})p_B$$

Both methods give similar rate laws.