

Kinetics and Reactor Design HW8

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Assigned: March 28, 2023

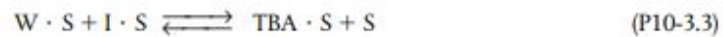
Due: April 6, 2023

1 Problem Statement

1.1 P10-3_A (a, c)

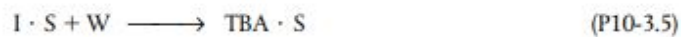
P10-3_A t-Butyl alcohol (TBA) is an important octane enhancer that is used to replace lead additives in gasoline [Ind. Eng. Chem. Res., 27, 2224 (1988)]. TBA was produced by the liquid-phase hydration (W) of isobutene (I) over an Amberlyst-15 catalyst. The system is normally a multiphase mixture of hydrocarbon, water, and solid catalysts. However, the use of cosolvents or excess TBA can achieve reasonable miscibility.

The reaction mechanism is believed to be



Derive a rate law assuming:

- (a) The surface reaction is rate-limiting.
- (b) The adsorption of isobutene is limiting.
- (c) The reaction follows Eley-Rideal kinetics

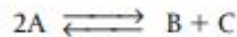


and the surface reaction is limiting.

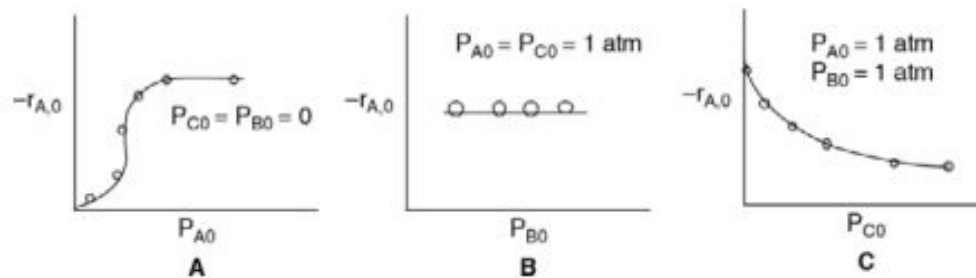
Figure 1

1.2 P10-4_B (a, b)

P10-4_B Consider the catalytic reaction as a function of the initial partial pressures



The rate of disappearance of species A was obtained in a differential reactor and is shown below.

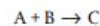


- (a) What species are on the surface?
 (b) What does Figure B tell you about the reversibility and what's adsorbed on the surface?

Figure 2

1.3 P10-12_B (a, b)

P10-12_B Experimental data for the gas-phase catalytic reaction



is shown below. The limiting step in the reaction is known to be irreversible, so that the overall reaction is irreversible. The reaction was carried out in a differential reactor to which A, B, and C were all fed.

Run Number	P_A (atm)	P_B (atm)	P_C (atm)	Reaction rate (mol)/(g-cat • s)
1	1	1	2	0.114
2	1	10	2	1.140
3	10	1	2	0.180
4	1	20	2	2.273
5	1	20	10	0.926
6	20	1	2	0.186
7	0.1	1	2	0.0243

- (a) Suggest a rate law consistent with the experimental data. *Hint:* Sketch $(-r'_A)$ as a function of P_A , as a function of P_B , and as a function of P_C .
 (b) From your rate expression, which species can you conclude are adsorbed on the surface?

Figure 3

2 Problem Solution

2.1 P10-3_A (a, c)

a) We are told the surface reaction is rate limiting. Therefore we care about Equation P10-3.3, as it is the one that is rate limiting.

$$\frac{r_{ADI}}{k_A} = 0 \quad (1)$$

$$\frac{r_{ADW}}{k_A} = 0 \quad (2)$$

$$\frac{r_D}{k_D} = 0 \quad (3)$$

$$C_{IS} = K_I C_I C_V \quad (4)$$

$$C_{WS} = K_W C_W C_V \quad (5)$$

$$C_{TBAS} = \frac{C_{TBA} C_V}{K_D} = C_{TBA} C_V K_{TBA} \quad (6)$$

$$r_s = k_s \left[C_{WS} C_{IS} - \frac{C_{TBAS} C_V}{K_S} \right] \quad (7)$$

$$r_s = k_s \left[K_I C_I C_V \times K_W C_W C_V - \frac{C_{TBA} C_V K_{TBA} C_V}{K_S} \right] \quad (8)$$

$$r_s = k_s K_I K_W C_V^2 \left[C_W C_I - \frac{C_{TBA}}{K_P} \right] \quad (9)$$

$$K_P = \frac{K_S K_I K_W}{K_{TBA}} \quad (10)$$

$$C_T = C_V + C_{IS} + C_{WS} + C_{TBAS} = C_V (1 + K_I C_I + K_W C_W + K_{TBA} C_{TBA}) \quad (11)$$

$$-r'_I = -r'_W = r_s = \frac{k_s K_I K_W C_T^2 \left[C_W C_I - \frac{C_{TBA}}{K_P} \right]}{(1 + K_I C_I + K_W C_W + K_{TBA} C_{TBA})^2} \quad (12)$$

c) With Elay-Rideal kinetics, we basically have the same question but without C_{WS} and with C_W in the rate law instead.

$$r_s = k_s \left[C_W C_{IS} - \frac{C_{TBAS}}{K_S} \right] \quad (13)$$

$$C_{IS} = K_I C_I C_V \quad (14)$$

$$C_{TBAS} = \frac{C_{TBA} C_V}{K_D} = C_{TBA} C_V K_{TBA} \quad (15)$$

$$C_T = C_V + C_{IS} + C_{TBAS} = C_V (1 + K_I C_I + K_{TBA} C_{TBA}) \quad (16)$$

$$r_s = k_s K_I C_V \left[C_I C_W - \frac{C_{TBA}}{K_H} \right] \quad (17)$$

$$K_H = \frac{K_S K_I}{K_{TBA}} \quad (18)$$

$$-r_I' = \frac{k_s K_I C_T \left[C_I C_W - \frac{C_{TBA}}{K_H} \right]}{1 + K_I C_I + K_{TBA} C_{TBA}} \quad (19)$$

2.2 P10-4_B (a, b)

a) Partial pressure of B doesn't have an effect on the rate of disappearance of species A, whereas pressures of A and C do. Therefore A and C are on the surface.

b) Figure B shows that the reaction is irreversible, because increasing partial pressure of B does not decrease the rate of disappearance, thus meaning that adding more product will not cause A to appear or even disappear slower.

2.3 P10-12_B (a, b)

4 runs possible for P_A (P_B and P_C are constant at 1 atm and 2 atm respectively). It looks like this:

2.4 P10-4_B (a, b)

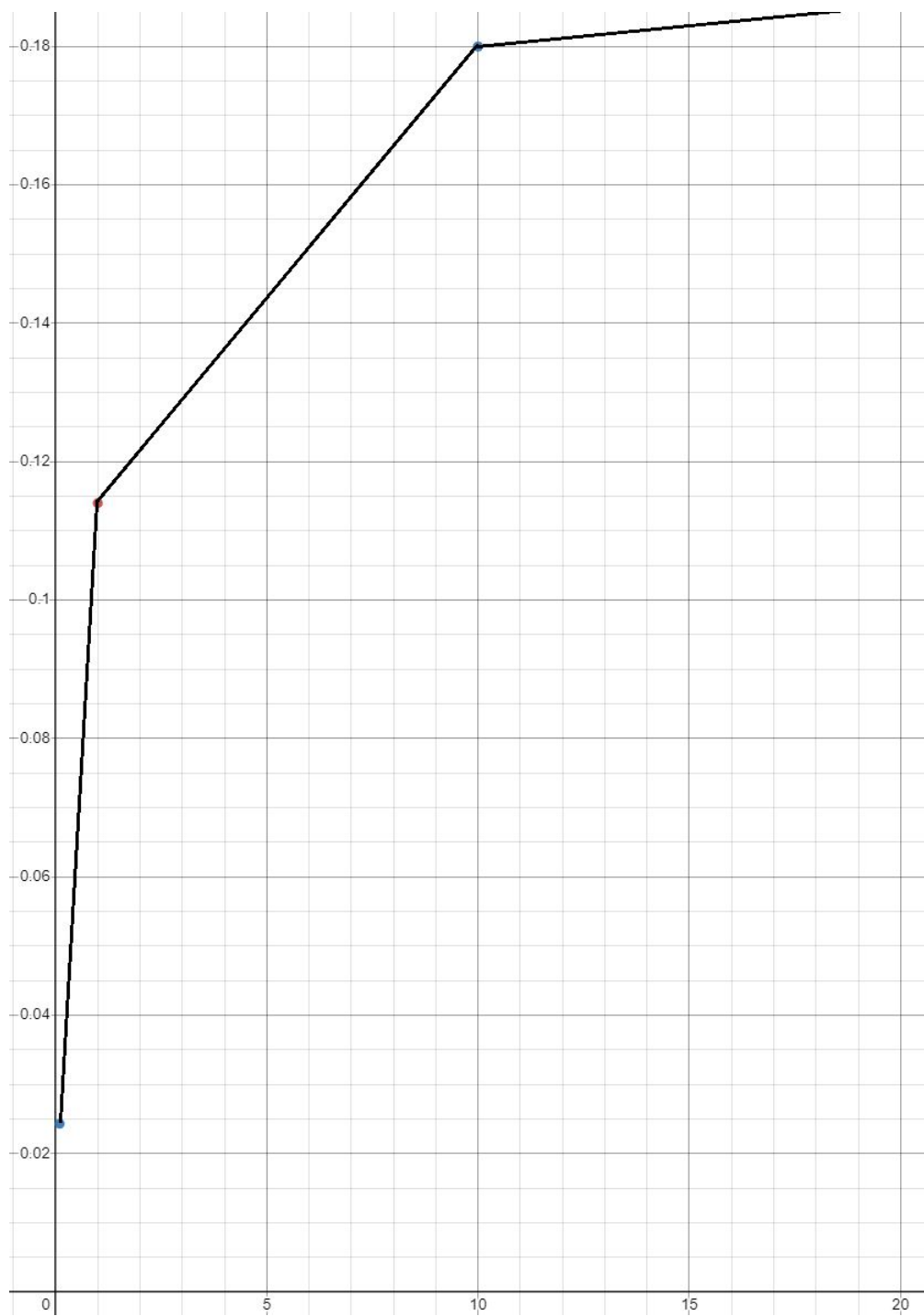


Figure 4: My graph for reaction rate as a function of P_A

In a similar vein, there are 3 runs possible for P_B (where the other two pressures are once again constants) and two for P_C . Those pictures are included below, respectively.

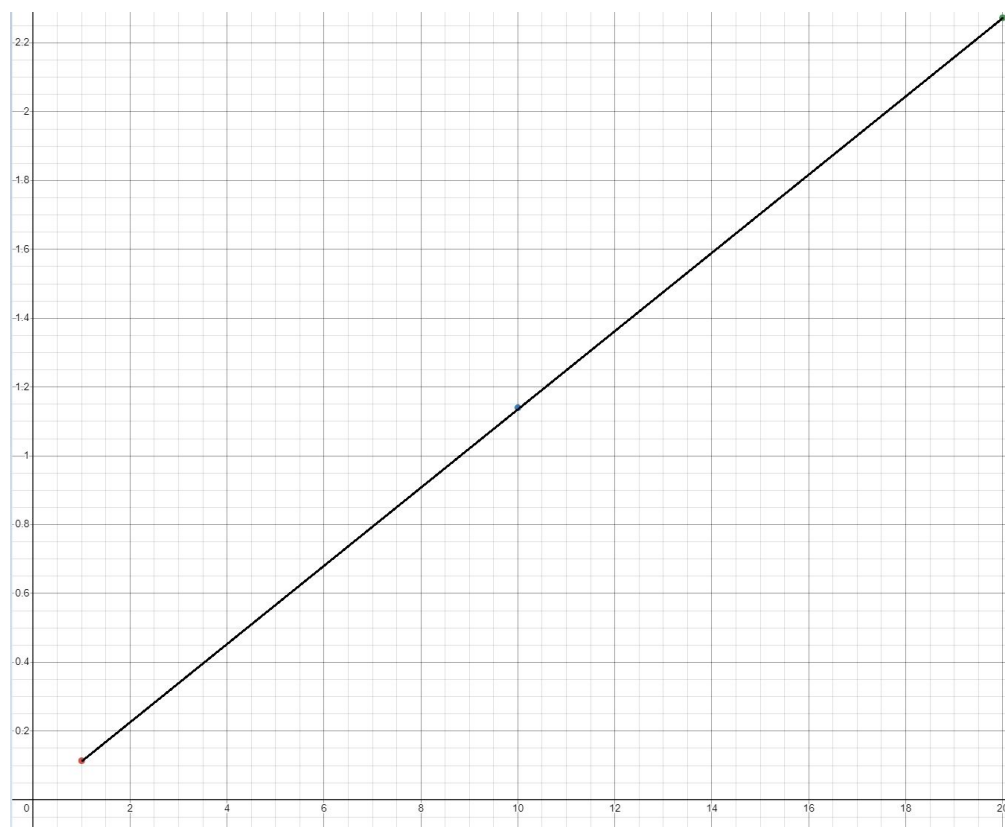


Figure 5: My graph for reaction rate as a function of P_B

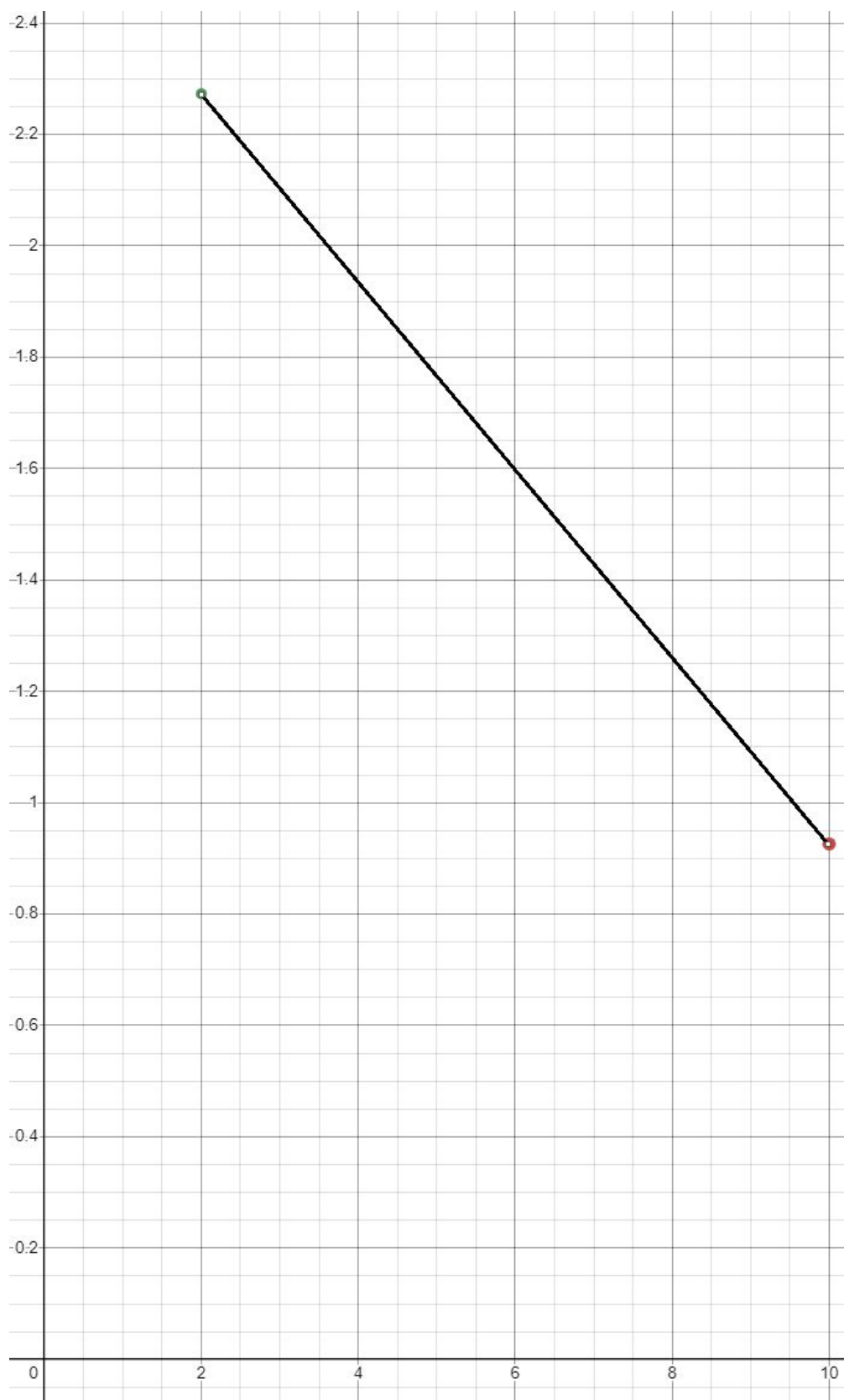


Figure 6: My graph for reaction rate as a function of P_C

A likely reaction law from the plots would be:

$$-r'_A = \frac{kP_AP_B}{1 + K_AP_A + K_CP_C} \quad (20)$$

A is definitely on the surface, as a higher concentration of A causes reaction rate to flatten out because all the catalyst sites are occupied. B is not on the surface, as adding it simply increases the reaction rate, so it's not being bound to any sites. High concentration of C decreases reaction rate, which means C is probably attached to the catalyst and preventing A from reacting by diminishing the number of available sites. So A and C are on the surface.