Tutorial 1

Reaction Kinetics

Chem 313

Ex. 1

For the reaction,

$$MnO_4^- + Fe^{2+} + H^+ \rightarrow Mn^{2+} + Fe^{3+} + H_2O$$

at a particular time, the production rate of Fe^{3+}, $\left(\frac{d[Fe^{3+}]}{dt} = 5.0 \times 10^{-2}\ mol\ L^{-1} s^{-1}\right)$. At the same moment, the rate of MnO_4^- consumption should be ------- mol L^{-1} s^{-1}

Solution

First of all check the (mass & charge) equation balancing

$$MnO_4^- + Fe^{2+} + H^+ \rightarrow Mn^{2+} + Fe^{3+} + H_2O$$

You may need to separate the anodic and cathodic reactions before writing the overall reaction.

$$\mathbf{MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O}$$

$$\mathbf{Fe^{2+} \rightarrow Fe^{3+} + e^-} \qquad \times 5$$

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Write the relation of the different rates

$$\frac{-d[MnO_4^-]}{dt} = \frac{d[Fe^{3+}]}{5dt} = \frac{5.0 \times 10^{-2}\ mol\ L^{-1}s^{-1}}{5}$$

$$\frac{-d[MnO_4^-]}{dt} = 1.0 \times 10^{-2}\ mol\ L^{-1}s^{-1}$$

Ex. 2

If the following equilibrium was interrupted by lowering the temperature, the new equilibrium should be sustained at ----------

$$A\ (g) + B\ (g) \rightleftharpoons C\ (g) + D\ (g) + \text{Heat}$$

a) the same equilibrium constant
b) the same equilibrium position
c) a higher [A] and [B]
d) a lower rate for the forward reaction

Solution

d) a lower rate for the forward reaction

Ex. 3

The reaction

$$A\,(g) + B\,(g) \rightleftharpoons C\,(g)$$

is second order with respect to A and zero order with respect to B. If 2 mol A and 3 mol B are mixed in a closed container of a fixed volume (V_1) at a given temperature (r_1 & k_1) and next the reaction was repeated with the same quantities at the same temperature but in another container of volume (V_2) (r_2 & k_2) where ($V_2 < V_1$), the following relation should be correct. r=the reaction rate, k=rate constant.

(a) $k_1 > k_2$	**(b) $r_1 > r_2$**	**(c) $r_2 = r_1$**	**(d) $k_1 = k_2$**

Solution

d) $k_1 = k_2$

Ex. 4

The activation energy of exothermic irreversible reactions is always ------

(a) negative	(b) positive	(c) 0	(d) missing information

Solution

d) positive

Ex. 5

The role of a catalyst is to change ---------- of the reaction.

(a) Gibbs energy
(b) equilibrium constant
(c) Heat
(d) activation energy

Solution

d) activation energy

Ex. 6

The average rate and instantaneous rate of a reaction are ---------.

(a) equal at the early start of the reaction
(b) equal at the end of the reaction
(c) equal in the middle of the reaction
(d) never equal unless two rates have a time interval equal to zero

Solution

d) never equal unless two rates have a time interval equal to zero

Ex. 7

The reaction A + 2B → products has been found to have the rate law, rate = $k[A]^2$. While holding the concentration of A constant, the concentration of B is increased from x to 3x. Predict by what factor the rate of reaction increases.

(a) 1	(b) 3	(c) 9	(d) 27

Solution

(a) 1

Ex. 8

For the first-order reaction A→Product, it took 284 min to attain 90 % completion of the reaction at 25°C. How long (in min) approximately will it take for the concentration of the reactant A to drop from 0.4 to 0.2 mol L^{-1}?

(a) 13.3	(b) 42.2	(c) 85.5	(d) 284.3

Solution

$$t = 284\ min$$

$$ln\frac{[A]_t}{[A]_0} = -kt$$

$$ln\frac{0.1[A]_0}{[A]_0} = -(k \times 284\ min)$$

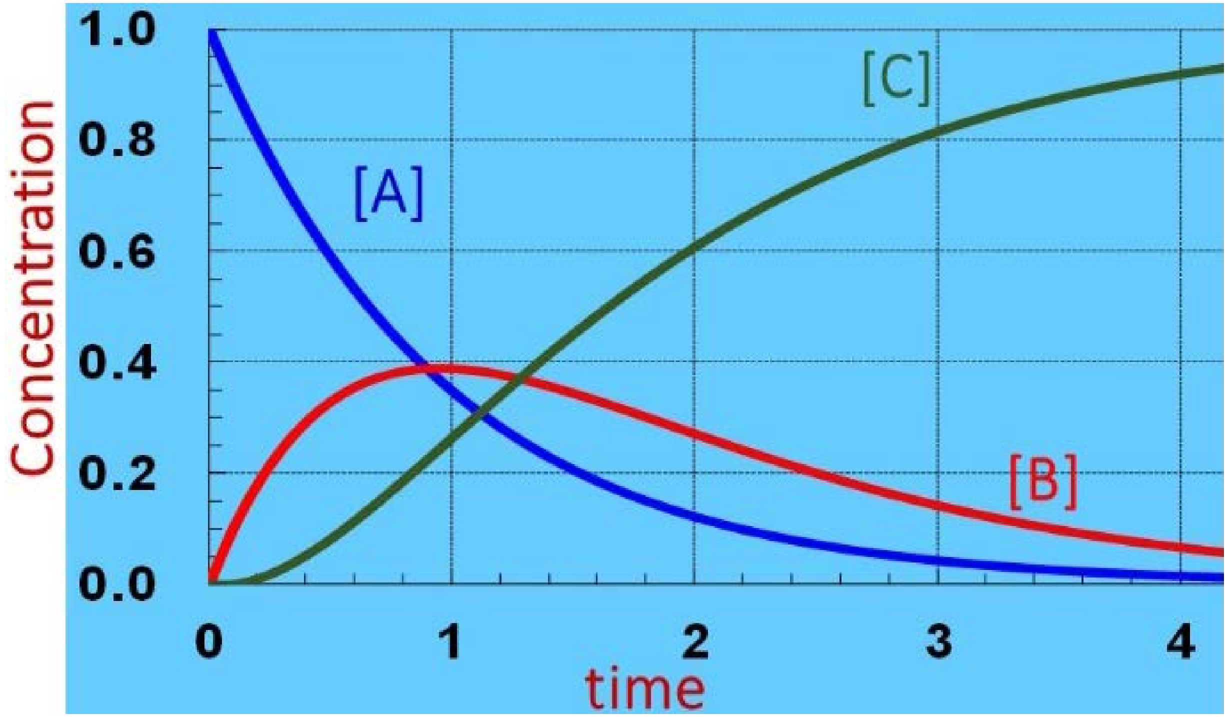
$$k = 8.12 \times 10^{-3}\ min^{-1}$$

$$ln\frac{0.2}{0.4} = -\left(8.12 \times 10^{-3}\ min^{-1}\right)t$$

(c) 85.5

Ex. 9

The following concentration profile may be suitable for ------ reactions



(a) parallel	(b) consecutive	(c) reversible	(d) independent

Solution

(a) consecutive

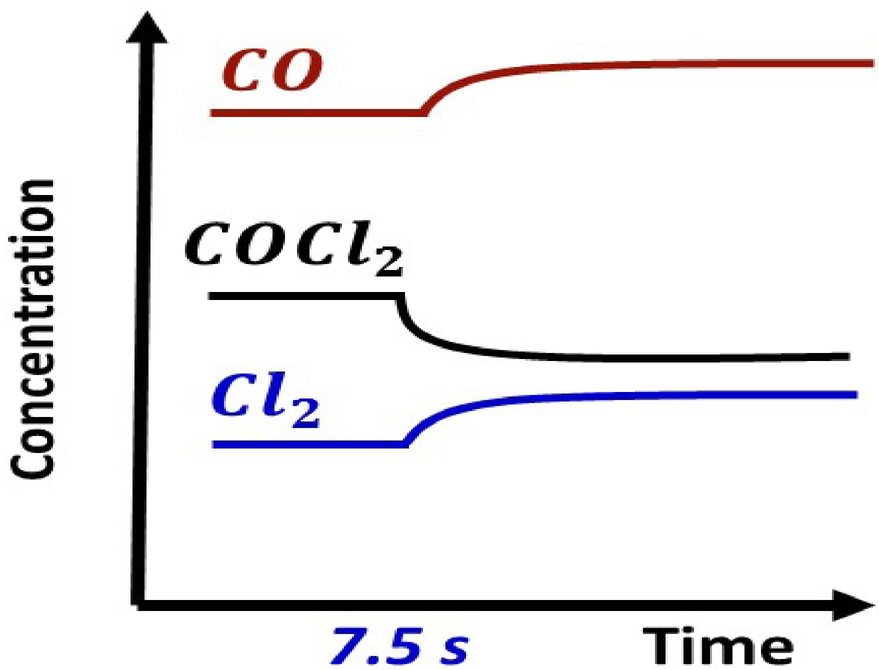
Ex. 10

For the following equilibrium

$$Cl_2(g) + CO(g) \rightleftharpoons COCl_2(g) \ \ \Delta H = -108kJ,$$

the following concentration profile was recorded. Guess: what did it disturb the equilibrium at t= 7.5 min?

(a) addition of $CO + Cl_2$	(c) increasing reactor volume
(b) removal of $COCl_2$	(d) heating up the reactor



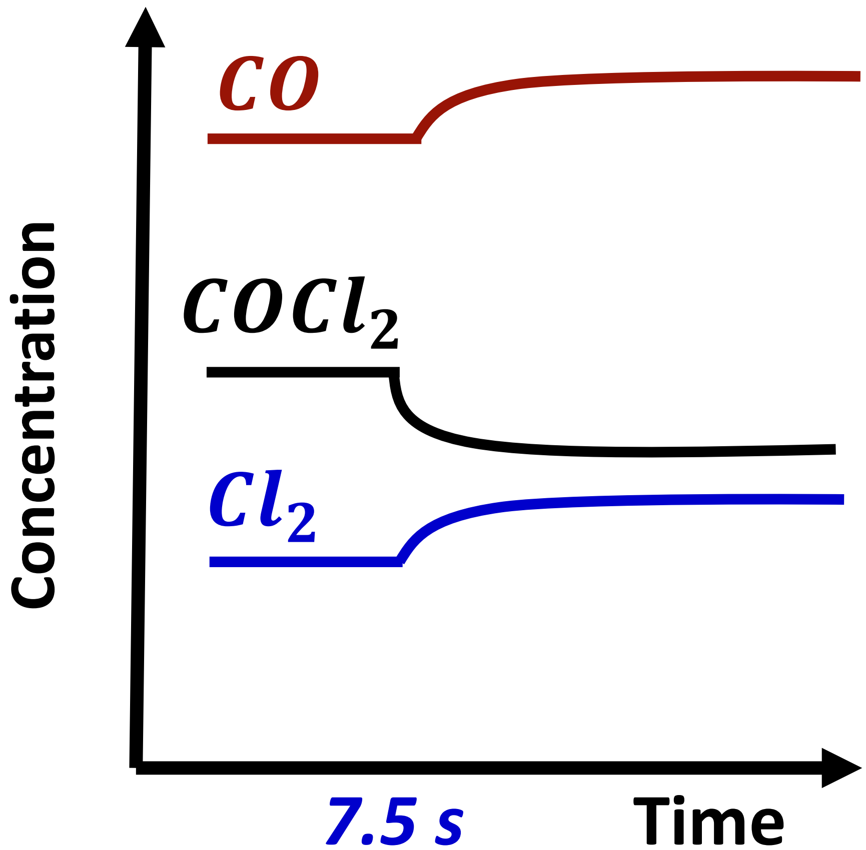
Solution

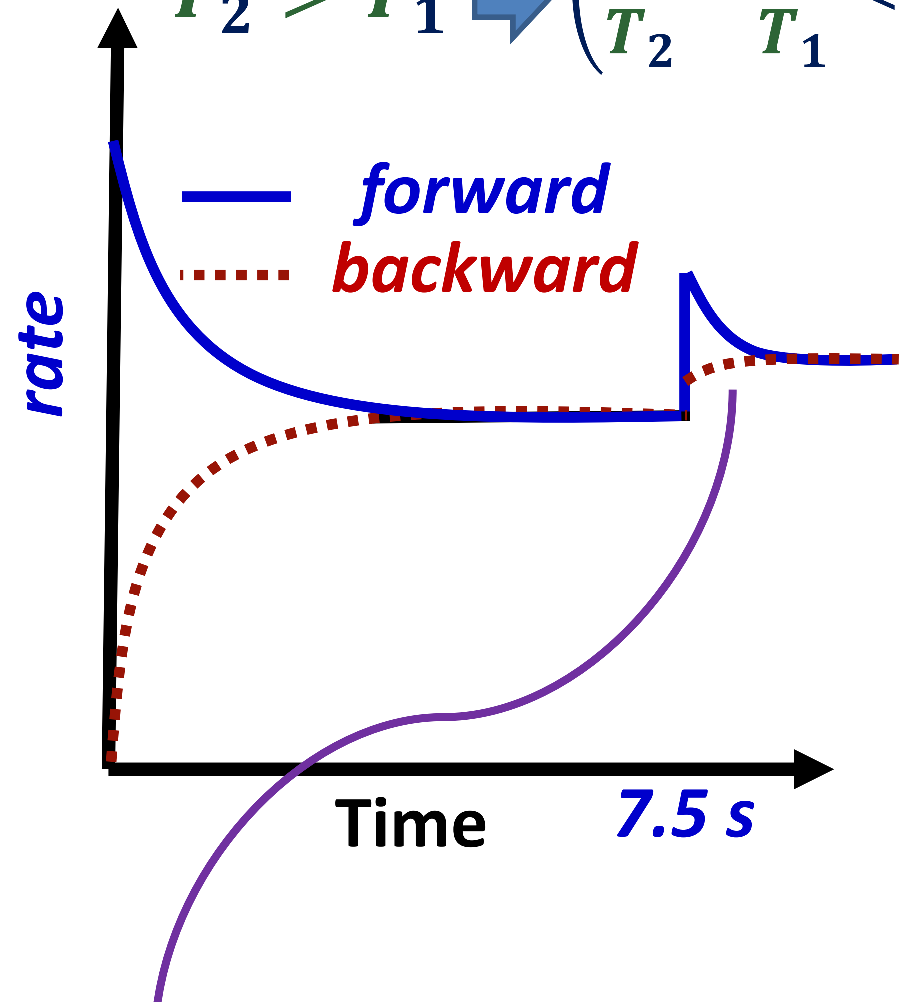
(d) heating up the reactor

Effect of heating

$$CO(g) + Cl_2(g) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} COCl_2(g) + Heat$$

$$T_2 > T_1 \Rightarrow \left(\frac{1}{T_2} - \frac{1}{T_1} < 0\right)$$





- ✓ *Both of the decrease in forward rate and increase in backward rate lead to accumulation of CO + Cl_2*

Ex. 11

The basic hydrolysis of ester was carried while keeping the initial concentration of the ester and NaOH the same at 0.02 mol L^{-1} at 35°C. The specific rate constant was 5.55 $mol^{-1}\ L\ min^{-1}$. Calculate the percent of ester that can be hydrolyzed in 30 min? Also calculate the time required for 30 % decomposition of ester?

Solution

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5\mathrm{OH}$$

Look at the k unit: It is a 2nd order reaction

Same Stoichiometry & same initial concentration

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + 2kt$$

In 30 min

$$\frac{1}{[A]_t} = \frac{1}{0.02\ mol\ L^{-1}} + 2\left(5.55\ mol^{-1} L\ min^{-1}\right)30\ min$$

$$[A]_t = 2.6 \times 10^{-3}\ mol\ L^{-1}$$

$$\text{Percent remaining} = \frac{[A]_t \times 100}{[A]_0} = 13.1\ \%$$

$$\text{Percent completion} = 100 - 13.1 = 86.9\%$$

Same Stoichiometry & same initial concentration

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + 2kt$$

For 30 % hydrolysis = 70% remaining

$$\text{Percent} = \frac{[A]_t \times 100}{[A]_0} = 70\ \%$$

$$\text{Percent} = \frac{[A]_t \times 100}{0.02\ mol\ L^{-1}} = 70\ \%$$

$$[A]_t = 0.014\ mol\ L^{-1}$$

$$\frac{1}{0.014\ mol\ L^{-1}} = \frac{1}{0.02\ mol\ L^{-1}} + 2(5.55\ mol^{-1} L\ min^{-1})t\ min$$

$$t = 1.93\ min$$