**Exercise 1.** Indicate which of the following statements are TRUE or FALSE:

a) For a reaction with a very large equilibrium constant, the rate constant of the forward reaction is much higher than the rate constant of the reverse reaction.

b) At equilibrium, the rate constants of the forward and reverse reactions are equal.

c) Increasing the concentration of a reactant increases the rate of a reaction by increasing the rate constant in the forward direction.

d) Increasing the concentration of a product, increases the rate of the reverse reaction, and so the rate of the forward reaction must then increase, too.

e) If $Q < K_{eq}$, the reaction will proceed towards generating more products until equilibrium is reached.

**Solution:**

a) True (This is true, given that $Keq = k_{for} / k_{rev}$)

b) False (The forward and reverse rates are equal, but the rate constants remain unchanged)

c) False (The rate constant does not get increased since it is a constant)

d) True (The system will try to reach equilibrium, where the rates of forward and reverse reactions need to be the same. So increased reverse reaction rate also leads to increased forward reaction)

e) True (See lecture 11, Slide 39)

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**Exercise 2.** Consider a reaction in which reactant R is converted into a product P at constant temperature. If the initial concentration of R is 1 mol/L, the half-life is 10 minutes. If the initial concentration is doubled, the half-life is two times lower.

a) What is the order of this reaction?

b) What is the rate constant of this reaction?

**Solution:**

a) Based on the text you can already notice that the time of half-life ($\tau_{1/2}$) depends on the initial concentration of the reactant. That means that it cannot be 1st order (constant). If we look at the equation for the 2nd order reactions:

$$\tau_{1/2} = \frac{1}{k[R]_0}$$

Increasing the $[R]_0$ by a factor of 2 ($[R]_0' = 2 \cdot [R]_0$) would reduce the $\tau_{1/2}$ by a factor of 2. The described reaction behavior is consistent with the 2nd order.

b) Given that $[R]_0 = 1$ mol/L and $\tau_{1/2} = 10$ min, and for reactions of the 2nd order we have:

$$\tau_{1/2} = \frac{1}{k[R]_0}$$

If we rearrange the equation and solve for k:

$$k = \frac{1}{\tau_{1/2}[R]_0} = \frac{1}{10 \cdot 1} \text{ L mol}^{-1} \cdot \text{min}^{-1} = 0.1 \text{ L mol}^{-1} \cdot \text{min}^{-1} = 1.67 \cdot 10^{-3} \text{ L mol}^{-1} \cdot \text{s}^{-1}$$

**Exercise 3.** Consider the following decomposition reaction:

$Ni(CO)_4(g) \rightarrow Ni(s) + 4\ CO(g)$

a) How is the rate of $Ni(CO)_4$ consumption related to the rate of CO production? Provide the equation.

b) If the rate of CO production is $2.4 \cdot 10^{-3}$ mol $L^{-1}$ $min^{-1}$ what is the rate of $Ni(CO)_4$ consumption at the same moment.

**Solution:**

a) Based on the stoichiometric coefficients:

$$-\frac{d[\mathrm{Ni(CO)_4}]}{dt} = \frac{1}{4}\frac{d[\mathrm{CO}]}{dt}$$

Or in words, the rate of $Ni(CO)_4$ consumption equals to ¼ of the rate of CO production.

b) Given the information from text we have:

$$\frac{d[\mathrm{CO}]}{dt} = 2.4 \times 10^{-3}\ \mathrm{mol\ L^{-1}min^{-1}}$$

Which if we connect to a) leads to:

$$-\frac{d[\mathrm{Ni(CO)_4}]}{dt} = \frac{1}{4}(2.4 \times 10^{-3}\ \mathrm{mol\ L^{-1}min^{-1}}) = 6.0 \times 10^{-4}\ \mathrm{mol\ L^{-1}min^{-1}}$$

Or in seconds:

$$6.0 \times 10^{-4}\ \mathrm{mol\ L^{-1}min^{-1}} \times \frac{1\ \mathrm{min}}{60\ \mathrm{s}} = 1.0 \times 10^{-5}\ \mathrm{mol\ L^{-1}s^{-1}}$$

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**Exercise 4.** You are studying the kinetics of the following reaction:

$2\ NO(g) + 2\ H_2(g) \rightarrow N_2(g) + 2\ H_2O(l)$

And by changing the ratio of starting reactant concentrations, the following experimental results were obtained:

| Measurement # | $[NO]_0$ ($mol^{-1}L^{-1}$) | $[H_2]_0$ ($mol^{-1}L^{-1}$) | Rate of $N_2$ production (mol $L^{-1}$ $min^{-1}$) |
|---|---|---|---|
| 1 | 1.0 | 1.0 | 0.15 |
| 2 | 1.0 | 2.0 | 0.30 |
| 3 | 1.0 | 3.0 | 0.45 |
| 4 | 2.0 | 3.0 | 1.80 |
| 5 | 3.0 | 3.0 | 4.05 |

a) Determine the partial reaction order for each reactant.

b) Determine the global reaction order for the entire reaction.

c) Write the equation that describes the reaction rate as a function of NO and $H_2$ concentrations?

**Solution:**

a) From the table we can observe that:

- When comparing measurements 1, 2, and 3: The initial concentration of NO is kept constant, while the initial concentration of $H_2$ is increased by a factor of 2 (measurement 2) and 3 (measurement 3), compared to measurement 1. As a consequence, the resulting rate of $N_2$ production increases 2-fold in measurement 2 and 3-fold in measurement 3.

$$[H_2]_0^2 / [H_2]_0^1 = 2 \quad \rightarrow \quad v_2 / v_1 = 2$$

$$[H_2]_0^3 / [H_2]_0^1 = 3 \quad \rightarrow \quad v_3 / v_1 = 3$$

This is consistent with the 1st order dependence $\mathbf{v \sim k \bullet [H_2]^1}$

- When comparing measurements 3,4, and 5: The initial concentration of $H_2$ is kept constant, while the initial concentration of NO is increased by a factor of 2 (measurement 4) and 3 (measurement 5), compared to measurement 3. As a consequence the resulting rate of $N_2$ production increases 4-fold in measurement 4 and 9-fold in measurement 5.

$$[NO]_0^4 / [NO]_0^3 = 2 \quad \rightarrow \quad v_4 / v_3 = 4$$

$$[NO]_0^5 / [NO]_0^3 = 3 \quad \rightarrow \quad v_5 / v_3 = 9$$

This is consistent with the 2nd order dependence $\mathbf{v \sim k \bullet [NO]^2}$

b) The global reaction order is the sum of partial reaction orders for each reactant: **2 + 1 = 3**

c) The final equation is: $\mathbf{v = k \bullet [H_2]^1 \bullet [NO]^2}$

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**Exercise 5.** Consider the decomposition reaction below:

$$N_2O_5(g) \rightarrow 2\ NO_2(g) + \tfrac{1}{2}\ O_2(g)$$

The reaction takes place at T = 318 K, with the rate constant of $5.0 \cdot 10^{-4}\ s^{-1}$. The activation energy for this reaction is 100 kJ/mol.

a) What is the order of this reaction?

b) What percentage of the starting amount of $N_2O_5(g)$ decomposes after 45 min at 318 K?

c) Calculate the rate constant at 332 K.

d) What is the time of half-life at 332 K?

Given values: $R = 8.314\ J\ K^{-1}\ mol^{-1}$

**Solution:**

a) If just looking at the reaction, this is actually ambiguous (can be any order). However, based on the unit of the reaction constant ($s^{-1}$) we can conclude that it is 1st order.

b) Given that the $k_{318} = 5.0 \cdot 10^{-4}$ $s^{-1}$ and considering the integrated rate law for 1st order reactions:

$$[A](t) = [A]_0 e^{-kt}$$

The fraction decomposing at any point in time (t) can be calculated as the $[A]_{rem} = ([A]_0 - [A]_{(t)}) / [A]_0 = 1 - [A]_{(t)} / [A]_0$, since $[A]_0$ represents the starting amount of material and $[A]_{(t)}$ represents the remaining amount of material. In this case:

$$[A]_{decomp} = 1 - \frac{[A](t)}{[A]_0} = 1 - e^{-kt} = 1 - e^{-(5.0\times10^{-4})(2700)} = 1 - e^{-1.35} \approx 0.7408$$

So, 74.08% of the original amount of $N_2O_5$ will be decomposed.

c) A default approach to calculate this would be to first determine the Arrhenius constant (A) using the known $k_1$, $T_1$, and activation energy ($E_a$). Then you can use the value of A, $E_a$ and $T_2$ to calculate the $k_2$.

However, there is also a shortcut. If we write Arrhenius equation for 2 temperatures:

$$k_1 = Ae^{-E_a/(RT_1)}, \qquad k_2 = Ae^{-E_a/(RT_2)}$$

And divide them to get the ratio of $k_2/k_1$:

$$\frac{k_2}{k_1} = \frac{Ae^{-E_a/(RT_2)}}{Ae^{-E_a/(RT_1)}} = e^{-E_a/(RT_2)+E_a/(RT_1)} = e^{-\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

Then you can calculate the $k_2$ as:

$$k_2 = k_1 \exp\left[-\frac{E_a}{R}\left(\frac{1}{332} - \frac{1}{318}\right)\right] = 5.0 \times 10^{-4} \times \exp(1.59497) \approx 2.46 \times 10^{-3}\ \mathrm{s}^{-1}$$

d) For 1st order reactions we have:

$$t_{1/2} = \frac{\ln 2}{k_2} = \frac{\ln 2}{2.46 \times 10^{-3}} \approx 281\ \mathrm{s} \approx 4.69\ \mathrm{min}$$

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**Exercise 6.** Consider a chemical reaction in which reactant A is converted into product B following first-order kinetics. At the start of the reaction, the initial concentration of A is: $[A]_0$=0.1 mol/L. After 1 hour at 25°C, 40% of reactant A has been converted into product B. To speed up the process, the temperature of the reaction mixture is then raised to 35°C and the reaction is continued for 1 more hour. After this time interval (1 h at 25°C + 1 h at 35°C) it is observed that the concentration of A is equal to 0.01 mol/L.

a) Calculate the rate constant of this reaction at 25°C and at 35°C.

b) Calculate the temperature at which you must continue this reaction so that only $10^{-3}$ mol/L of A remains in the reaction mixture after an additional 30 minutes of reaction. *Hint*: You may have to first calculate the rate constant of the reaction at that temperature and its activation energy.

Given values: R = 8.314 J $K^{-1}$ $mol^{-1}$

**Solution:**

a) If we consider 1st order reaction, we can rearrange the reaction to determine k:

$$[A](t) = [A]_0 e^{-kt} \quad \Rightarrow \quad k = -\frac{1}{t} \ln \frac{[A](t)}{[A]_0}$$

From the text we have that after 1 hour (=3600s) of reaction time at 25˚C, the concentration of A dropped from 0.10 mol/L to 0.06 mol/L (40% reduction). If we use these values to calculate the $k_{25}$:

$$k_{25} = -\frac{1}{3600} \ln \frac{0.060}{0.100} = -\frac{1}{3600} \ln(0.6) = 1.41896 \times 10^{-4}\ \mathrm{s}^{-1}$$

Next, the reaction proceeds for 1 more hour at 35˚C further reducing the content of A to 0.01 mol/L. From there we can calculate the $k_{35}$:

$$k_{35} = -\frac{1}{3600} \ln \frac{0.010}{0.060} = -\frac{1}{3600} \ln(1/6) = 4.97711 \times 10^{-4}\ \mathrm{s}^{-1}$$

b) Here we can apply a similar trick as in solution 5 c) to calculate the ratio of $k_{35}/k_{25}$:

$$\ln \frac{k_{35}}{k_{25}} = -\frac{E_a}{R}\left(\frac{1}{T_{35}} - \frac{1}{T_{25}}\right)$$

From here we can determine the activation energy for this reaction:

$$E_a = -R \frac{\ln(k_{35}/k_{25})}{(1/T_{35} - 1/T_{25})} = 95.9\ \mathrm{kJ\ mol}^{-1}$$

And, knowing that the reaction needs to reduce the concentration of A from 0.01 mol/L to 0.001 mol/L in 30 min, we can determine the $k_{req}$:

$$k_{\mathrm{req}} = -\frac{1}{1800} \ln \frac{1.0 \times 10^{-3}}{0.010} = -\frac{1}{1800} \ln(0.1) = 1.27921 \times 10^{-3}\ \mathrm{s}^{-1}$$

Next, you can either proceed to calculate the Arrhenius constant (*A*), or you can use the ratio of k values and avoid the Arrhenius constant altogether. This second approach is shown below:

$$\ln \frac{k_{\mathrm{req}}}{k_{25}} = -\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{25}}\right) \longrightarrow \frac{1}{T} = \frac{1}{T_{25}} - \frac{R}{E_a} \ln \frac{k_{\mathrm{req}}}{k_{25}}$$

Given that the values for $k_{25}$, $E_a$, $T_{25}$, and R are all known we ultimately get:

$$\frac{1}{T} = \frac{1}{298.15} - 1.91 \times 10^{-4} = 3.164 \times 10^{-3}\ \mathrm{K}^{-1}$$

$$T = \frac{1}{3.164 \times 10^{-3}} \approx 316\ \mathrm{K} = 42.9^{\circ}\mathrm{C}$$

**Exercise 7.** Consider the following second-order reaction:

$$A \rightarrow 2\,B$$

Assume that the volume and temperature do not change during the reaction. For the following initial conditions, $[A]_0$ = 0.5 mol/L and $[B]_0$ = 0 mol/L, it is observed that the half-life of A is 15 min.

a) Calculate the rate constant (k).

b) Assuming that the same reaction described in the text above is still running, calculate the reaction rate (v) at the time point when the concentration of B increases to [B] = 0.5 mol/L.

c) Assuming that the same reaction described in the text above is still running, calculate the time needed for the concentration of B to increase from [B] = 0.5 mol/L to [B] = 0.8 mol/L.

**Solution:**

a) Given that it is a 2nd order reaction for A, we assume:

$$v = -\frac{d[A]}{dt} = k[A]^2$$

For a 2nd order reaction the time of half-life is given as:

$$t_{1/2} = \frac{1}{k[A]_0}$$

The values for both, time of half-life and initial concentration are given. So we can solve for k:

$$k = \frac{1}{t_{1/2}[A]_0} = \frac{1}{(15\ \mathrm{min})(0.50\ \mathrm{mol\,L^{-1}})} = \frac{1}{7.5\ \mathrm{min}} = 1.33 \times 10^{-1}\ \mathrm{L\,mol^{-1}\,min^{-1}}$$

Or if we use second instead of minutes: $k = 2.22 \times 10^{-3}\ \mathrm{Lmol^{-1}s^{-1}}$

b) Relate [A] and [B] by stoichiometry. Starting with $[B]_0 = 0$:

$$[B] = 2([A]_0 - [A]) \quad \Rightarrow \quad [A] = [A]_0 - \tfrac{1}{2}[B]$$

If [B] = 0.50 mol/L then the remaining amount of [A] is 0.25 mol/L. So if we use that concentration value in the equation for v given above:

$$v = (1.33 \times 10^{-1})(0.25)^2 = 0.1333 \times 0.0625 = 8.33 \times 10^{-3}\ \mathrm{mol\,L^{-1}\,min^{-1}}$$

Or if we use second instead of minutes: $v = 1.39 \times 10^{-4}\ \mathrm{mol\ L^{-1}s^{-1}}$

c) If B changes from [B] = 0.50 mol/L to [B] = 0.80 mol/L, the change in A can be followed using reaction stoichiometry from the chemical equation. Over the corresponding time range: [A] changed from 0.25 mol/L to 0.1 mol/L. Here we can apply the integrated version of the rate law for 2nd order reactions:

$$\frac{1}{[A](t)} - \frac{1}{[A]_0} = kt$$

If we re-arrange we get:

$$t = \frac{1}{k}\left(\frac{1}{[A]_{(t)}} - \frac{1}{[A]_0}\right)$$

To go from concentration $[A]_1 = 0.25$ mol/L to $[A]_2 = 0.1$ mol/L

$$\Delta t = \frac{1}{k}\left(\frac{1}{[A]_2} - \frac{1}{[A]_1}\right) \quad \rightarrow \quad \Delta t = \frac{6}{0.133333} = 45 \text{ min}$$

You can also do the same calculation by using the real $[A]_0 = 0.5$ mol/L and determining the time needed to get from 0.5 to 0.1 mol/L, and then subtracting the time needed to get from 0.5 to 0.25 mol/L. It is perhaps a "cleaner" application of the equation for $2^{nd}$ order reaction kinetics since both times you would be starting from the true $[A]_0$.

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**Exercise 8.** You are characterizing the reversible reaction below:

$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftarrows FeSCN^{2+}(aq)$

The equilibrium constant for this reaction at 25˚C is K=140. In 1.0 L of water at 25 °C you prepare the following combination of reagents:

$[Fe^{3+}]_0 = 0.20$ mol/L
$[SCN^{-}]_0 = 0.10$ mol/L

a) Is the system in equilibrium? If not, in which direction will the reaction proceed?

b) Calculate the equilibrium concentrations of all species?

**Solution:**

a) Here you can just notice that there is no product in solution at time point 0. Therefore, the chemical system cannot be in equilibrium. But more formally, we can calculate the value of Q:

$$Q = \frac{[\mathrm{FeSCN}^{2+}]_0}{[\mathrm{Fe}^{3+}]_0[\mathrm{SCN}^-]_0} = \frac{0}{0.20 \times 0.10} = 0$$

And since Q=0, it is lower than K=140, so we can conclude that the system is not in equilibrium and that the reaction will move towards generating more products ($FeSCN^{2+}$).

b) Let's assume that $x = [FeSCN^{2+}]_{eq}$. Then by stoichiometry:

$$[\mathrm{FeSCN}^{2+}]_{\mathrm{eq}} = x,$$
$$[\mathrm{Fe}^{3+}]_{\mathrm{eq}} = 0.20 - x,$$
$$[\mathrm{SCN}^-]_{\mathrm{eq}} = 0.10 - x.$$

Now we can apply these values in the equilibrium constant equation for this reaction:

$$K = \frac{[\mathrm{FeSCN}^{2+}]_{\mathrm{eq}}}{[\mathrm{Fe}^{3+}]_{\mathrm{eq}}[\mathrm{SCN}^-]_{\mathrm{eq}}} = \frac{x}{(0.20 - x)(0.10 - x)} = 140$$

This produces a quadratic equation:

$$140x^2 - 43x + 2.8 = 0$$

Which has 2 solutions:

$$x_1 = \frac{43 - 16.763}{280} = \frac{26.237}{280} \approx 0.0937 \text{ M},$$
$$x_2 = \frac{43 + 16.763}{280} = \frac{59.763}{280} \approx 0.2134 \text{ M}.$$

The second solution ($x_2$) is physically not possible due to the fact that this amount is higher than the maximum possible amount, determined by the starting reactants: $[SCN^-]_0 = 0.1$ mol/L. $x_1$ does satisfy this requirement as it is lower than the theoretical maximum amount of product that can be made.

So, if we take $x_1$ as the solution we get:

$$[\text{FeSCN}^{2+}]_{\text{eq}} = x = 0.0937 \text{ mol/L}$$
$$[\text{Fe}^{3+}]_{\text{eq}} = 0.20 - x = 0.20 - 0.0937 = 0.1063 \text{ mol/L}$$
$$[\text{SCN}^-]_{\text{eq}} = 0.10 - x = 0.10 - 0.0937 = 0.0063 \text{ mol/L}$$

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**Exercise 9.** You are interested in developing cleaning products based on hydrogen peroxide ($H_2O_2$). However, most water sources will have small amounts of iron oxide (rust), which can catalyze degradation of $H_2O_2$. From the literature, you find that the activation energy for spontaneous decomposition of $H_2O_2$ is 75.3 kJ/mol and in the presence of iron oxide, that value is reduced to 67.8 kJ/mol. This change seems relatively small, but you still want to check the impact on the rate constant.

What is the ratio of $H_2O_2$ decomposition rates in the presence and absence of iron oxide?

Given values:

$R = 8.314$ J $K^{-1}$ $mol^{-1}$
T = 25˚C

**Solution:**

Here, we first start by considering the Arrhenius' equations for the two processes:

$$k_{\text{uncat}} = A\, e^{-E_{a,\text{uncat}}/(RT)} \qquad k_{\text{cat}} = A\, e^{-E_{a,\text{cat}}/(RT)}$$

If we then divide them to calculate the ratio of catalyzed vs uncatalyzed reactions:

$$\frac{k_{\text{cat}}}{k_{\text{uncat}}} = \frac{A\, e^{-E_{a,\text{cat}}/(RT)}}{A\, e^{-E_{a,\text{uncat}}/(RT)}} = \exp\left(\frac{E_{a,\text{uncat}} - E_{a,\text{cat}}}{RT}\right)$$

Here, we just apply the numbers and we will get the solution:

$$\frac{k_{\text{cat}}}{k_{\text{uncat}}} \approx 20.6$$

Make sure that you always use temperature values in K (=298K in this case).

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**Exercise 10.** Below are two examples of reaction cascades involving iodine (1st reaction followed by a 2nd). Does iodine act as a catalyst in either cascade reaction? Explain.

a) $S_2O_8^{2-}(aq) + 2\,I^-(aq) \rightarrow I_2(aq) + 2\,SO_4^{2-}(aq)$ : $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

b) $2\,I^-(aq) + Cl_2(aq) \rightarrow I_2(aq) + 2\,Cl^-(aq)$ : $6\,ClO^-(aq) + I_2(aq) \rightarrow 2\,IO_3^-(aq) + 6\,Cl^-(aq)$

**Solution:**

a) Yes, iodine acts as a catalyst. $I^-$ is consumed in the first reaction to form $I_2$, but $I_2$ is fully converted back to $I^-$ in the second reaction, so iodine species are regenerated and end the overall process unchanged.

b) No, iodine is not a catalyst here. $I^-$ is converted to $I_2$ in the first reaction, but in the second reaction $I_2$ is further oxidized to $IO_3^-$, so the iodine species are not regenerated and therefore do not function catalytically.

Quick Answers:

1.

a) True

b) False

c) False

d) True

e) True

2.

a) $2^{nd}$ order

b) $k = 0.1\ L\ mol^{-1}\ min^{-1}$

3.

a) $v = -\frac{d[Ni(CO)4]}{dt} = +\frac{1}{4}\frac{d[CO]}{dt}$

b) $6 \cdot 10^{-4}\ mol\ L^{-1}\ min^{-1}$

4.

a) 1 for $H_2$; 2 for NO;

b) 3 for the entire reaction;

c) $v = k\ [NO]^2[H_2]$;

5.

a) $1^{st}$ order

b) 74.08% decomposes

c) $2.5 \cdot 10^{-3}\ s^{-1}$

d) $t_{1/2} = 277.26$ s

6.

a) $k_1$ (25˚C) = $1.42 \cdot 10^{-4}\ s^{-1}$ ; $k_2$ (35˚C) = $4.98 \cdot 10^{-4}\ s^{-1}$ ;
b) T3 = 316 K (42.9°C) ; k3 (42.9˚C) = $1.28 \cdot 10^{-3}\ s^{-1}$ ; $E_a$ = 95.4 kJ/mol ;

7.

a) $k = 0.133\ L\ mol^{-1}\ min^{-1}$ (or $2.22 \times 10^{-3}\ L\ mol^{-1}\ s^{-1}$)
b) $v = 8.31 \cdot 10^{-3}\ mol\ L^{-1}\ s^{-1}$ (or $1.39 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}$)
c) t = 45 min

8.

a) No; The reaction will proceed towards the generation of products.

b) $[FeSCN^{2+}]_{eq}$ = 0.094 mol/L ; $[Fe^{3+}]_{eq}$ = 0.106 mol/L ; $[SCN^-]_{eq}$ = 0.006 mol/L ;

9.

$K_{(iron\text{-}oxide)}/k_{(alone)} = 20.6$

10.

a) Yes. It is regenerated by the $2^{nd}$ reaction

b) No. The $2^{nd}$ reaction just makes a new species.