

Chemistry 2000B Spring 2002 Assignment 2 Solutions

1. If 95% has decayed, 5% remains, i.e. $x/x_0 = 0.05$. For a first-order reaction,

$$\begin{aligned}\frac{x}{x_0} &= \left(\frac{1}{2}\right)^{t/t_{1/2}} \\\therefore \ln\left(\frac{x}{x_0}\right) &= \frac{t}{t_{1/2}} \ln\left(\frac{1}{2}\right) \\\therefore t &= t_{1/2} \frac{\ln(x/x_0)}{\ln(1/2)} \\&= (5.3\text{s}) \frac{\ln(0.05)}{\ln(1/2)} = 23\text{s}.\end{aligned}$$

2. (a) We can calculate the rate constant from the half-life by $k = \ln 2/t_{1/2}$. The results at the two temperatures are as follows:

T ($^{\circ}\text{C}$)	T (K)	k (min^{-1})
140	413.15	0.0154
180	453.15	0.0347

According to the Arrhenius equation, $k = k_{\infty} e^{-E_a/(RT)}$. Therefore

$$\begin{aligned}\frac{k_{180}}{k_{140}} &= \frac{e^{-E_a/(453.15R)}}{e^{-E_a/(413.15R)}} = \exp\left(-\frac{E_a}{453.15R} + \frac{E_a}{413.15R}\right) \\\therefore \ln\left(\frac{k_{180}}{k_{140}}\right) &= \frac{E_a}{R} \left(\frac{1}{413.15\text{K}} - \frac{1}{453.15\text{K}}\right) \\\therefore E_a &= \frac{(8.314510\text{JK}^{-1}\text{mol}^{-1}) \ln\left(\frac{0.0347\text{min}^{-1}}{0.0154\text{min}^{-1}}\right)}{\frac{1}{413.15\text{K}} - \frac{1}{453.15\text{K}}} \\&= 31.6\text{kJ/mol}.\end{aligned}$$

To get the preexponential factor, we rearrange the Arrhenius equation to $k_{\infty} = k e^{E_a/(RT)}$. We can use either of the data points. For instance,

$$k_{\infty} = 0.0347\text{min}^{-1} \exp\left(\frac{31.6 \times 10^3\text{J/mol}}{(8.314510\text{JK}^{-1}\text{mol}^{-1})(453.15\text{K})}\right) = 150\text{min}^{-1}.$$

(b) This is a very similar exercise to question 1:

$$t = t_{1/2} \frac{\ln(x/x_0)}{\ln(1/2)} = (20 \text{ min}) \frac{\ln\left(\frac{1 \text{ mg/kg}}{13 \text{ mg/kg}}\right)}{\ln(1/2)} = 74 \text{ min.}$$

Meat fried at 180°C for 74 min would look, smell, feel and taste like shoe leather, so this isn't a really practical way to get the benzylpenicillin levels down to acceptable levels.

3. At equilibrium for this reaction,

$$\begin{aligned} k_+[A] &= k_-[B]^2. \\ \therefore \frac{[B]^2}{[A]} &= K = \frac{k_+}{k_-}. \\ \therefore k_- &= \frac{k_+}{K} = \frac{13 \text{ s}^{-1}}{1.3 \times 10^{13} \text{ mol/L}} = 1.0 \times 10^{-12} \text{ L mol}^{-1} \text{ s}^{-1}. \end{aligned}$$

4. First, we have to calculate the pressures of all the reactants and products using the ideal gas law. For instance,

$$\begin{aligned} n_{\text{HCl}} &= \frac{20 \text{ g}}{36.4606 \text{ g/mol}} = 0.55 \text{ mol.} \\ \therefore P_{\text{HCl}} &= \frac{nRT}{V} = \frac{(0.55 \text{ mol})(8.314510 \text{ J K}^{-1} \text{ mol}^{-1})(673.15 \text{ K})}{2 \times 10^{-3} \text{ m}^3} = 1.5 \times 10^6 \text{ Pa} \equiv 15 \text{ atm.} \end{aligned}$$

The activity of HCl is therefore $a_{\text{HCl}} = 15 \text{ atm}/1 \text{ atm} = 15$. Proceeding similarly, we get

	n (mol)	P (Pa)	a
O ₂	0.25	7.0×10^5	6.9
Cl ₂	0.85	2.4×10^6	23
H ₂ O	0.67	1.9×10^6	18

The equilibrium constant is therefore

$$K = \frac{(a_{\text{Cl}_2})^2(a_{\text{H}_2\text{O}})^2}{(a_{\text{HCl}})^4(a_{\text{O}_2})} = \frac{(23)^2(18)^2}{(15)^4(6.9)} = 0.51.$$

5. (a) Under these conditions,

$$Q = \frac{a_{\text{HI}}^2}{(a_{\text{H}_2})(a_{\text{I}_2})} = \frac{a_{\text{HI}}^2}{a_{\text{H}_2}} = \frac{0.300^2}{0.400} = 0.225.$$

Since $Q < K$, the reaction must proceed from left to right (hydrogen and iodine combine into hydrogen iodide) to reach equilibrium.

(b) Let x the amount of H_2 used, expressed as an activity (proportional to pressure in atm).

	a_{H_2}	a_{HI}
Initial	0.400	0.300
Final	$0.400 - x$	$0.300 + 2x$

The equilibrium condition becomes

$$K = 0.352 = \frac{a_{\text{HI}}^2}{a_{\text{H}_2}} = \frac{(0.300 + 2x)^2}{0.400 - x}.$$

$$\therefore 0.352(0.400 - x) = (0.300 + 2x)^2 = 0.0900 + 1.20x + 4x^2.$$

$$\therefore 0 = 4x^2 + 1.552x - 0.0508.$$

This last equation is solved using the quadratic equation:

$$x = \frac{-1.552 \pm \sqrt{1.552^2 - 4(4)(-0.0508)}}{2(4)} = \frac{-1.552 \pm 1.795}{8}.$$

We know that x , the amount of H_2 used, has to be positive. Therefore, we must take the positive sign in the above equation:

$$x = \frac{-1.552 + 1.795}{8} = 0.030.$$

The final pressures of the two gases are therefore

$$P_{\text{H}_2} = 0.4 - 0.030 \text{ atm} = 0.370 \text{ atm},$$

$$\text{and } P_{\text{HI}} = 0.3 + 2(0.030) \text{ atm} = 0.361 \text{ atm}.$$

6. The reaction is $\text{N}_2\text{O}_{4(\text{g})} \rightleftharpoons 2\text{NO}_{2(\text{g})}$. The equilibrium constant is therefore $K = a_{\text{NO}_2}^2 / a_{\text{N}_2\text{O}_4}$. We need to find the pressures of the reactant and product to solve this problem. We know the initial number of moles of N_2O_4 :

$$n_{\text{N}_2\text{O}_4} = \frac{2.33 \text{ g}}{92.0110 \text{ g/mol}} = 0.0253 \text{ mol}.$$

$$\therefore P_{\text{N}_2\text{O}_4}^{(i)} = \frac{(0.0253 \text{ mol})(8.314510 \text{ J K}^{-1} \text{ mol}^{-1})(296.05 \text{ K})}{\frac{1296 \text{ cm}^3}{(100 \text{ cm/m})^3}} = 4.81 \times 10^4 \text{ Pa} \equiv 0.475 \text{ atm}.$$

The (total) equilibrium pressure (P) is 441 mm Hg, which is 0.580 atm. The total pressure is the sum of the partial pressures:

$$P = P_{\text{N}_2\text{O}_4} + P_{\text{NO}_2}.$$

Now let x be the amount (expressed as a pressure in atm) of N_2O_4 reacted, and consider the following table:

	$P_{\text{N}_2\text{O}_4} \text{ (atm)}$	$P_{\text{NO}_2} \text{ (atm)}$
Initial	0.475	0
Final	$0.475 - x$	$2x$

The final pressure (in atm) is therefore

$$P = (0.475 - x) + 2x = 0.475 + x = 0.580 \text{ atm.}$$

$$\therefore x = 0.106 \text{ atm.}$$

$$\therefore P_{\text{N}_2\text{O}_4} = 0.475 - 0.106 \text{ atm} = 0.369 \text{ atm,}$$

$$\text{and } P_{\text{NO}_2} = 2(0.106 \text{ atm}) = 0.211 \text{ atm.}$$

$$\therefore K = \frac{0.211^2}{0.369} = 0.121.$$