

# Chemistry 2000 Spring 2001 Section B Test 1 Solutions

1. (a) We first compare experiments 1 and 2. At constant  $[\text{O}_2]$ , the concentration of NO is doubled, resulting in a (roughly) fourfold increase in the rate. Thus, the order with respect to  $[\text{NO}]$  is 2. Experiments 1 and 3 were carried out at identical NO concentrations but the oxygen concentration in experiment 3 was double that in experiment 1. The rate also doubled, so the order with respect to  $[\text{O}_2]$  is 1. The rate law is therefore

$$\text{rate} = k[\text{O}_2][\text{NO}]^2.$$

- (b) We should get similar values using any of the three experiments. From the first, we get

$$k = \frac{\text{rate}}{[\text{O}_2][\text{NO}]^2} = \frac{2.8 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}}{(0.0010 \text{ mol/L})(0.0020 \text{ mol/L})^2} = 7.0 \times 10^3 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}.$$

2. 1 L of solution contains 9.919 mol of ethanol and weighs 913.9 g. The molar mass of ethanol is 46.068 g/mol. Thus

$$m_{\text{eth}} = (9.919 \text{ mol})(46.068 \text{ g/mol}) = 456.9 \text{ g}.$$

The rest (457.0 g) is water. The molar mass of water is 18.015 g/mol so the number of moles of water is

$$n_{\text{H}_2\text{O}} = \frac{457.0 \text{ g}}{18.015 \text{ g/mol}} = 25.368 \text{ mol}.$$

The mole fraction of ethanol is therefore

$$X_{\text{eth}} = \frac{9.919 \text{ mol}}{9.919 + 25.368 \text{ mol}} = 0.2811.$$

3. By stoichiometry, if we start with 0.9 atm of dimethyl ether and form 0.7 atm of methane, we have used 0.7 atm of dimethyl ether. We thus have 0.2 atm left. We need to find  $t$  such that  $x = 0.2 \text{ atm}$  with  $x_0 = 0.9 \text{ atm}$ :

$$\begin{aligned} 0.2 \text{ atm} &= 0.9 \text{ atm} \left(\frac{1}{2}\right)^{t/1733\text{s}} \\ \therefore \frac{0.2}{0.9} &= 0.22 = \left(\frac{1}{2}\right)^{t/1733\text{s}} \\ \therefore \ln(0.22) &= \ln \left[ \left(\frac{1}{2}\right)^{t/1733\text{s}} \right] = \frac{t}{1733\text{s}} \ln \left(\frac{1}{2}\right) \\ \therefore t &= \frac{(1733\text{s}) \ln(0.22)}{\ln(1/2)} = 3786\text{s} \equiv 1 \text{ h } 3 \text{ min} \end{aligned}$$

4. If the reaction is first order, a plot of  $\ln[A]$  vs  $t$  should give a straight line. If the reaction is second order, a plot of  $1/[A]$  vs  $t$  should give a straight line. Conversely, if we use the wrong plot, the data will not fit a line.
5. We have a pair of equations in two unknowns:

$$\begin{aligned} 0.085 \text{ s}^{-1} &= k_{\infty} \exp\left(-\frac{E_a}{750R}\right) & (477^{\circ}\text{C} = 750 \text{ K}) \\ 140 \text{ s}^{-1} &= k_{\infty} \exp\left(-\frac{E_a}{1000R}\right) & (727^{\circ}\text{C} = 1000 \text{ K}) \end{aligned}$$

If we divide these two equations, we eliminate  $k_{\infty}$  and obtain a single equation in one unknown:

$$\begin{aligned} \frac{0.085}{140} = 6.07 \times 10^{-4} &= \frac{\exp\left(-\frac{E_a}{750R}\right)}{\exp\left(-\frac{E_a}{1000R}\right)} \\ &= \exp\left(-\frac{E_a}{750R} + \frac{E_a}{1000R}\right) \\ &= \exp\left[\frac{E_a}{R} \left(\frac{1}{1000 \text{ K}} - \frac{1}{750 \text{ K}}\right)\right] \\ &= \exp\left(-3.33 \times 10^{-4} \text{ K}^{-1} \frac{E_a}{R}\right) \\ \therefore \ln(6.07 \times 10^{-4}) = -7.41 &= -3.33 \times 10^{-4} \text{ K}^{-1} \frac{E_a}{R} \\ \therefore \frac{E_a}{R} &= 2.22 \times 10^4 \text{ K} \\ \therefore E_a &= (8.314510 \text{ J K}^{-1} \text{ mol}^{-1})(2.22 \times 10^4 \text{ K}) = 185 \text{ kJ/mol} \end{aligned}$$

To get  $k_{\infty}$ , we can go back to either of the original equations. For instance,

$$\begin{aligned} 0.085 \text{ s}^{-1} &= k_{\infty} \exp\left(-\frac{E_a}{750R}\right) = 1.35 \times 10^{-13} k_{\infty} \\ \therefore k_{\infty} &= 6.3 \times 10^{11} \text{ s}^{-1} \end{aligned}$$

6. (a)  $\frac{d[\text{HBr}]}{dt} = k_1[\text{H}][\text{Br}_2] - k_{-1}[\text{HBr}][\text{Br}]$

(b) At equilibrium,

$$\begin{aligned} \frac{d[\text{HBr}]}{dt} &= 0 \\ \therefore k_1[\text{H}][\text{Br}_2] &= k_{-1}[\text{HBr}][\text{Br}] \\ \therefore K &= \frac{[\text{HBr}][\text{Br}]}{[\text{H}][\text{Br}_2]} = \frac{k_1}{k_{-1}} \end{aligned}$$

(c)  $k_{-1} = k_1/K = 1.4 \times 10^{-20} \text{ L mol}^{-1} \text{ s}^{-1}$