

Chemistry 4000/5000/7001, Fall 2012, Assignment 1 Solutions

1. (a) Rate of reaction: $v = k[\text{NO}_3][\text{NO}]$
Order with respect to $[\text{NO}_3]$: 1 (exponent of $[\text{NO}_3]$ in rate law)
Overall order: 2 (sum of partial orders)

(b)

$$v = \frac{1}{2} \frac{d[\text{NO}_2]}{dt}$$
$$\therefore \frac{d[\text{NO}_2]}{dt} = 2k[\text{NO}_3][\text{NO}]$$

- (c) The rate of reaction has units of (change in concentration) over (time), or in the case described, v has units of molecules $\text{cm}^{-3} \text{s}^{-1}$.
From the rate law, we have

$$k = \frac{v}{[\text{NO}_3][\text{NO}]}$$

The units of k are therefore

$$\frac{\text{molecules cm}^{-3} \text{s}^{-1}}{(\text{molecules cm}^{-3})^2} = \text{cm}^3 \text{molecules}^{-1} \text{s}^{-1}.$$

(d) i.

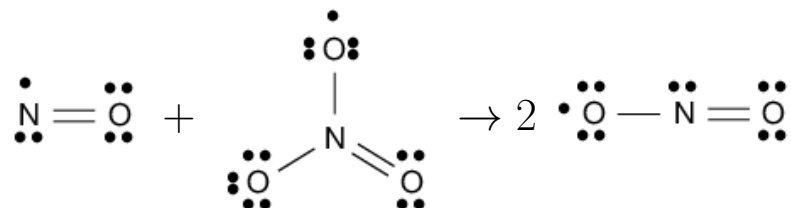
$$pV = nRT$$
$$\therefore \frac{n}{V} = \frac{p}{RT}$$

or $p = RT \frac{n}{V}$

n/V is the concentration. Either of the last two equations is sufficient to show that p and the concentration are proportional provided T is constant. (If the temperature isn't constant, the proportionality constant changes over the course of the experiment, so that the rate of change of p is no longer just proportional to the rate of change of the concentration.)

- ii. Units of rate: bar s^{-1}
 Units of rate constant: $\text{bar}^{-1}\text{s}^{-1}$

Bonus: The reaction is shown in Lewis structure form below:



(Note that NO_3 and NO_2 both have additional resonance structures.)

The reaction is very simple. Looking at the reactants and products, we see that we just need to transfer an oxygen atom (with its six electrons) from NO_3 to NO in order for this reaction to occur. This is the sort of simple process that can occur in a single step during a collision.

2. (a) The Arrhenius equation is

$$k = A \exp\left(-\frac{E_a}{RT}\right).$$

Apply this equation to two temperatures, T_1 and T_2 , then take the ratio of the rate constants:

$$\begin{aligned} \frac{k_2}{k_1} &= \frac{A \exp\left(-\frac{E_a}{RT_2}\right)}{A \exp\left(-\frac{E_a}{RT_1}\right)} \\ &= \exp\left(-\frac{E_a}{RT_2} + \frac{E_a}{RT_1}\right) \\ &= \exp\left[\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]. \end{aligned}$$

We want to know what value of E_a gives $k_2/k_1 = 2$ for T_1 and T_2 separated by 10 degrees. Take $T_1 = 298$ and $T_2 = 308$ K. (You

will get a slightly different answer if you pick a different pair of temperatures.) Then,

$$\begin{aligned}\ln\left(\frac{k_2}{k_1}\right) &= \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \\ \therefore E_a &= \frac{R \ln(k_2/k_1)}{\frac{1}{T_1} - \frac{1}{T_2}} \\ &= \frac{(8.314\,472\text{ J K}^{-1}\text{ mol}^{-1}) \ln(2)}{\frac{1}{298} - \frac{1}{308\text{ K}}} \\ &= 5.3 \times 10^4\text{ J mol}^{-1} \equiv 53\text{ kJ mol}^{-1}.\end{aligned}$$

To the extent that our rule of thumb is correct, 50 kJ mol^{-1} is a typical activation energy.

(b) Take $E_a = \frac{1}{2}(53\text{ kJ mol}^{-1}) \approx 26\text{ kJ mol}^{-1}$. Then,

$$\begin{aligned}\frac{k_2}{k_1} &= \exp\left[\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \\ &= \exp\left[\frac{26 \times 10^3\text{ J mol}^{-1}}{8.314\,472\text{ J K}^{-1}\text{ mol}^{-1}}\left(\frac{1}{298} - \frac{1}{308\text{ K}}\right)\right] \\ &= 1.4.\end{aligned}$$

A 10-degree increase in temperature would only increase the rate constant by a factor of 1.4.

(c) Now take $E_a = 2(53\text{ kJ mol}^{-1}) \approx 106\text{ kJ mol}^{-1}$.

$$\begin{aligned}\frac{k_2}{k_1} &= \exp\left[\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \\ &= \exp\left[\frac{106 \times 10^3\text{ J mol}^{-1}}{8.314\,472\text{ J K}^{-1}\text{ mol}^{-1}}\left(\frac{1}{298} - \frac{1}{308\text{ K}}\right)\right] \\ &= 4.\end{aligned}$$