

Solutions

Solution 1:

In the following exercises and problems, it is recommended that rate constants are labeled with the number of the step in the proposed reaction mechanism and that any reverse steps are labeled similarly but with a prime.

E23.1(b) The intermediates are NO and NO₃ and we apply the steady-state approximation to each of their concentrations

$$\begin{aligned}k_2 [\text{NO}_2] [\text{NO}_3] - k_3 [\text{NO}] [\text{N}_2\text{O}_5] &= 0 \\k_1 [\text{N}_2\text{O}_5] - k'_1 [\text{NO}_2] [\text{NO}_3] - k_2 [\text{NO}_2] [\text{NO}_3] &= 0 \\ \text{Rate} &= -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} \\ \frac{d[\text{N}_2\text{O}_5]}{dt} &= -k_1 [\text{N}_2\text{O}_5] + k'_1 [\text{NO}_2] [\text{NO}_3] - k_3 [\text{NO}] [\text{N}_2\text{O}_5]\end{aligned}$$

From the steady-state equations

$$\begin{aligned}k_3 [\text{NO}] [\text{N}_2\text{O}_5] &= k_2 [\text{NO}_2] [\text{NO}_3] \\ [\text{NO}_2] [\text{NO}_3] &= \frac{k_1 [\text{N}_2\text{O}_5]}{k'_1 + k_2}\end{aligned}$$

Substituting,

$$\begin{aligned}\frac{d[\text{N}_2\text{O}_5]}{dt} &= -k_1 [\text{N}_2\text{O}_5] + \frac{k'_1 k_1}{k'_1 + k_2} [\text{N}_2\text{O}_5] - \frac{k_2 k_1}{k'_1 + k_2} [\text{N}_2\text{O}_5] = -\frac{2k_1 k_2}{k'_1 + k_2} [\text{N}_2\text{O}_5] \\ \text{Rate} &= \frac{k_1 k_2}{k'_1 + k_2} [\text{N}_2\text{O}_5] = k [\text{N}_2\text{O}_5]\end{aligned}$$

Solution 2:

A₂ appears in the initiation step only.

$$\frac{d[\text{A}_2]}{dt} = -k_1 [\text{A}_2]$$

Consequently, the rate of consumption of [A₂] is first order in A₂ and the rate is independent of intermediate concentrations.

Solution 3:

The collision frequency is

$$z = \frac{2^{1/2} \sigma \langle \bar{c} \rangle p}{kT} \quad \text{where } \sigma = \pi d^2 = 4\pi r^2 \text{ and } \langle \bar{c} \rangle = \left(\frac{8RT}{\pi M} \right)^{1/2}$$

$$\begin{aligned} \text{so } z &= \frac{2^{1/2} p (4\pi r^2) \left(\frac{8RT}{\pi M} \right)^{1/2}}{kT} = \frac{16p N_A r^2 \pi^{1/2}}{(RTM)^{1/2}} \\ &= \frac{16 \times (100 \times 10^3 \text{ Pa}) \times (6.022 \times 10^{23} \text{ mol}^{-1}) \times (180 \times 10^{-12} \text{ m})^2 \times (\pi)^{1/2}}{[(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (28.01 \times 10^{-3} \text{ kg mol}^{-1})]^{1/2}} \\ &= \boxed{6.64 \times 10^9 \text{ s}^{-1}} \end{aligned}$$

The collision density is

$$Z_{AA} = \frac{1}{2} z N / V = \frac{zp}{2kT} = \frac{(6.64 \times 10^9 \text{ s}^{-1}) \times (100 \times 10^3 \text{ Pa})}{2(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})} = \boxed{8.07 \times 10^{34} \text{ m}^{-3} \text{ s}^{-1}}$$

Raising the temperature at constant volume means raising the pressure in proportion to the temperature

$$Z_{AA} \propto \sqrt{T}$$

so the percent increase in z and Z_{AA} due to a 10 K increase in temperature is 1.6 percent, same as Exercise 24.1(a).

Solution 4:

(a) A diffusion-controlled rate constant in decylbenzene is

$$k_d = \frac{8RT}{3\eta} = \frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{3 \times (3.36 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})} = \boxed{1.97 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

(b) In concentrated sulfuric acid

$$k_d = \frac{8RT}{3\eta} = \frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{3 \times (27 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})} = \boxed{2.4 \times 10^5 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

Solution 5:

The Gibbs energy of activation is related to the rate constant by

$$k_2 = B \exp\left(\frac{-\Delta^\ddagger G}{RT}\right) \quad \text{where } B = \frac{kRT^2}{hp^\ominus} \quad \text{so } \Delta^\ddagger G = -RT \ln \frac{k_2}{B}$$

$$\begin{aligned} k_2 &= (6.45 \times 10^{13} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) e^{-\{(5375 \text{ K})/(298 \text{ K})\}} = 9.47 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\ &= 947 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \end{aligned}$$

Using the value of B computed in Exercise 27.13(b), we obtain

$$\begin{aligned} \Delta^\ddagger G &= -(8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln \left(\frac{947 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}{1.54 \times 10^{11} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}} \right) \\ &= \boxed{46.8 \text{ kJ mol}^{-1}} \end{aligned}$$

Solution 6:

The number of collisions of gas molecules per unit surface area is

$$Z_W = \frac{N_A P}{(2\pi MRT)^{1/2}}$$

(a) For N_2

$$\begin{aligned} \text{(i)} \quad Z_W &= \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (10.0 \text{ Pa})}{(2\pi \times (28.013 \times 10^{-3} \text{ kg mol}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}))^{1/2}} \\ &= 2.88 \times 10^{23} \text{ m}^{-2} \text{ s}^{-1} \\ &= \boxed{2.88 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{(ii)} \quad Z_W &= \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (0.150 \times 10^{-6} \text{ Torr}) \times (1.01 \times 10^5 \text{ Pa}/760 \text{ Torr})}{(2\pi \times (28.013 \times 10^{-3} \text{ kg mol}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}))^{1/2}} \\ &= 5.75 \times 10^{17} \text{ m}^{-2} \text{ s}^{-1} \\ &= \boxed{5.75 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}} \end{aligned}$$

(b) For methane

$$\begin{aligned} \text{(i)} \quad Z_W &= \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (10.0 \text{ Pa})}{(2\pi \times (16.04 \times 10^{-3} \text{ kg mol}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}))^{1/2}} \\ &= 3.81 \times 10^{23} \text{ m}^{-2} \text{ s}^{-1} \\ &= \boxed{3.81 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{(ii)} \quad Z_W &= \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (0.150 \times 10^{-6} \text{ Torr}) \times (1.01 \times 10^5 \text{ Pa}/760 \text{ Torr})}{(2\pi \times (16.04 \times 10^{-3} \text{ kg mol}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}))^{1/2}} \\ &= 7.60 \times 10^{17} \text{ m}^{-2} \text{ s}^{-1} \\ &= \boxed{7.60 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}} \end{aligned}$$

Solution 7:

The Langmuir isotherm is

$$\theta = \frac{Kp}{1 + Kp} \quad \text{so} \quad p = \frac{\theta}{K(1 - \theta)}$$

$$\text{(a)} \quad p = \frac{0.20}{(0.777 \text{ kPa}^{-1}) \times (1 - 0.20)} = \boxed{0.32 \text{ kPa}}$$

$$\text{(b)} \quad p = \frac{0.75}{(0.777 \text{ kPa}^{-1}) \times (1 - 0.75)} = \boxed{3.9 \text{ kPa}}$$

Solution 8:

Langmuir isotherm is $\theta = Kp/(1 + Kp)$

We are looking for θ , so we must first find K or m_{mon}

$$K = \frac{\theta}{p(1 - \theta)} = \frac{m/m_{\text{mon}}}{p(1 - m/m_{\text{mon}})}$$

Setting this expression at one pressure equal to that at another pressure allows solution for m_{mon}

$$\frac{m_1/m_{\text{mon}}}{p_1(1 - m_1/m_{\text{mon}})} = \frac{m_2/m_{\text{mon}}}{p_2(1 - m_2/m_{\text{mon}})} \quad \text{so} \quad \frac{p_1(m_{\text{mon}} - m_1)}{m_1} = \frac{p_2(m_{\text{mon}} - m_2)}{m_2}$$

$$m_{\text{mon}} = \frac{p_1 - p_2}{p_1/m_1 - p_2/m_2} = \frac{(36.0 - 4.0) \text{ kPa}}{(36.0/0.63 - 4.0/0.21) \text{ kPa mg}^{-1}} = 0.84 \text{ mg}$$

$$\text{So } \theta_1 = 0.63/0.84 = \boxed{0.75} \quad \text{and} \quad \theta_2 = 0.21/0.84 = \boxed{0.25}$$