Chemistry 192
Recitation Section Problems
April 23, 2018
Solutions

1. A proposed mechanism for the reaction

$$NO_2Cl_{(g)} \longrightarrow NO_{2(g)} + \frac{1}{2}Cl_{2(g)}$$

is

$$NO_2Cl_{(g)} \xrightarrow{k_1} NO_{2(g)} + Cl_{(g)} \qquad \text{(fast)}$$

$$NO_{2(g)} + Cl_{(g)} \xrightarrow{k_{-1}} NO_2Cl_{(g)} \qquad \text{(fast)}$$

$$NO_2Cl_{(g)} + Cl_{(g)} \xrightarrow{k_2} NO_{2(g)} + Cl_{2(g)} \qquad \text{(slow)}$$

Use the steady-state approximation on the chlorine atom to derive the rate law associated with this mechanism.
Answer:

$$R = \frac{d[NO_2]}{dt} = k_2[NO_2Cl][Cl]$$

$$\frac{d[Cl]}{dt} = k_1[NO_2Cl] - k_{-1}[NO_2][Cl] - k_2[NO_2Cl][Cl]$$

$$= k_1[NO_2Cl] - [Cl](k_{-1}[NO_2] + k_2[NO_2Cl]) \approx 0$$

$$[Cl] = \frac{k_1[NO_2Cl]}{k_{-1}[NO_2] + k_2[NO_2Cl]}$$

$$R = \frac{k_1k_2[NO_2Cl]^2}{k_{-1}[NO_2] + k_2[NO_2Cl]} \approx \frac{k_1k_2[NO_2Cl]^2}{k_{-1}[NO_2]}$$

2. In the gas phase methylisocyanide (CH_3NC) converts to acetonitrile (CH_3CN) when heated. This type of reaction is called an isomerization reaction, because the product and reactant consist of the same atoms but are structurally different. Using structural formulas the reaction can be written

$$\mathrm{CH_3 - N \equiv C_{(g)} \longrightarrow CH_3 - C \equiv N_{(g)}}$$

A plausible mechanism for this reaction is

$$\mathrm{2CH_3NC_{(g)}} \xrightarrow{k_1} \mathrm{CH_3NC_{(g)} + CH_3NC^*_{(g)}} \qquad \text{(fast)}$$

$$\mathrm{CH_3NC_{(g)} + CH_3NC^*_{(g)}} \xrightarrow{k_{-1}} \mathrm{2CH_3NC_{(g)}} \qquad \text{(fast)}$$

$$\mathrm{CH_3NC^*_{(g)}} \xrightarrow{k_2} \mathrm{CH_3CN_{(g)}} \qquad \text{(slow)}$$

where CH_3NC^* represents a reactive intermediate that can facilely rearrange to product. Use the steady-state approximation to derive the rate law for the overall reaction.

Answer:

$$R = \frac{d[\mathrm{CH_3CN}]}{dt} = k_2[\mathrm{CH_3NC^*}]$$

$$\frac{d[\mathrm{CH_3NC^*}]}{dt} = k_1[\mathrm{CH_3NC}]^2 - k_{-1}[\mathrm{CH_3NC}][\mathrm{CH_3NC^*}] - k_2[\mathrm{CH_3NC^*}] \approx 0$$

$$k_1[\mathrm{CH_3NC}]^2 = [\mathrm{CH_3NC^*}](k_2 + k_{-1}[\mathrm{CH_3NC}])$$

$$[\mathrm{CH_3NC^*}] = \frac{k_1[\mathrm{CH_3NC}]^2}{k_2 + k_{-1}[\mathrm{CH_3NC}]}$$

$$R = \frac{k_1 k_2[\mathrm{CH_3NC}]^2}{k_2 + k_{-1}[\mathrm{CH_3NC}]}$$

Using $k_2 << k_{-1}$

$$R = \frac{k_1 k_2}{k_{-1}}[\mathrm{CH_3NC}]$$

3. Write out the following nuclear reactions

a. $^{234}_{92}\mathrm{U}$ decays emitting an alpha particle.

Answer:

$$^{234}_{92}\mathrm{U} \longrightarrow ^{4}_{2}\mathrm{He} + ^{230}_{90}\mathrm{Th}$$

b. $^{80}_{33}\mathrm{As}$ decays emitting a beta particle

Answer:

$$^{80}_{33}\mathrm{As} \longrightarrow ^{0}_{-1}\beta + ^{80}_{34}\mathrm{Se}$$

c. $^{246}_{96}\mathrm{Cm}$ reacts with $^{12}_{6}\mathrm{C}$ to produce $^{254}_{102}\mathrm{No}$ and sufficient neutrons to balance the reaction.

Answer:

$$^{246}_{96}\mathrm{Cm} + ^{12}_{6}\mathrm{C} \longrightarrow ^{254}_{102}\mathrm{No} + 4^{1}_{0}\mathrm{n}$$

d. $^{40}_{19}$K decays by positron emission.
Answer:

$$^{40}_{19}\text{K} \longrightarrow ^{0}_{+1}\beta + ^{40}_{18}\text{Ar}$$

e. $^{236}_{92}$U produces 3 neutrons, $^{141}_{55}$Cs plus another element (you must identify it).
Answer:

$$^{236}_{92}\text{U} \longrightarrow 3^{1}_{0}\text{n} + ^{141}_{55}\text{Cs} + ^{92}_{37}\text{Rb}$$

4. Complete the following nuclear reactions by identifying the species represented by a "?"
a.

$$^{3}_{1}\text{H} \longrightarrow ^{0}_{-1}\beta + ?$$

Answer:$^{3}_{2}$He

b.

$$? \longrightarrow ^{0}_{+1}\beta + ^{90}_{41}\text{Nb}$$

Answer:$^{90}_{42}$Mo

c.

$$^{217}_{91}\text{Pa} \longrightarrow ^{213}_{89}\text{Ac} + ?$$

Answer:$^{4}_{2}$He

d.

$$^{1}_{0}\text{n} + ^{235}_{92}\text{U} \longrightarrow ^{141}_{56}\text{Ba} + 4^{1}_{0}\text{n} + ?$$

Answer:$^{91}_{36}$Kr

e.

$$^{238}_{92}\text{U} + ? \longrightarrow ^{246}_{99}\text{Es} + 6^{1}_{0}\text{n}$$

Answer: $^{14}_{7}$N