Chemistry 192
Recitation Section Problems
April 16, 2018
Solutions

1a. Cyclobutane (C_4H_8) decomposes to form ethylene (C_2H_4) when heated according to the balanced reaction

$$C_4H_{8(g)} \longrightarrow 2C_2H_{4(g)}.$$

At time $t = 0$ a reaction vessel is filled with pure cyclobutane gas, and the volume and temperature are kept constant. The reaction is known to be first order with a rate constant $k = 2.48 \times 10^{-4}\ \mathrm{s}^{-1}$. Calculate the half life of the reactant.

Answer:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{2.48 \times 10^{-4}\ \mathrm{s}^{-1}} = 2.79 \times 10^3\ \mathrm{s}$$

1b. If the initial concentration of cyclobutane is 4.00×10^{-2} M, calculate the time at which the concentration of cyclobutane is 3.6×10^{-2} M.

Answer:

$$\ln \frac{[C_4H_8]_t}{[C_4H_8]_0} = -kt$$

$$\ln \frac{3.6 \times 10^{-2}}{4.00 \times 10^{-2}} = (-2.48 \times 10^{-4}\ \mathrm{s}^{-1})t$$

$$t = 4.2 \times 10^2\ \mathrm{s}$$

1c. Calculate the time necessary for the concentration of the ethylene (the product) to reach 1.00×10^{-2} M.

Answer:

At time t the concentration of ethylene is 1.00×10^{-2} M. From the stoichiometry of the reaction, at time t $[C_4H_8]_t = 4.00 \times 10^{-2}$ M - 0.500×10^{-2} M $= 3.50 \times 10^{-2}$ M. Then

$$\ln \frac{3.50 \times 10^{-2}}{4.00 \times 10^{-2}} = (-2.48 \times 10^{-4}\ \mathrm{s}^{-1})t$$

$$t = 5.38 \times 10^2\ \mathrm{s}$$

1d. Let P_0 be the initial pressure in the reaction vessel. First predict whether the total pressure in the vessel must increase or decrease with increasing time. Then derive an expression for the total pressure as a function of P_0, k and the time t.
Answer:
Because 2 moles of ethylene are formed for every mole of cyclobutane that dissociates, the pressure must increase with time. Let n_0 be the initial number of moles of cyclobutane introduced into the vessel. Then

	$n_{C_4H_8}$	$n_{C_2H_4}$
initial	n_0	0
change	$-\alpha n_0$	$2\alpha n_0$
final	$n_0(1-\alpha)$	$2\alpha n_0$

$$n_{tot} = n_{C4H_8} + n_{C_2H_4} = n_0(1+\alpha)$$

$$P_0 = \frac{n_0 RT}{V}$$

$$P_{tot} = \frac{n_{tot}RT}{V} = \frac{n_0(1+\alpha)RT}{V} = P_0(1+\alpha)$$

Letting n be the number of moles of cyclobutane at time t

$$n = n_0 e^{-kt}$$

$$n_0(1-\alpha) = n_0 e^{-kt}$$

or

$$\alpha = 1 - e^{-kt}$$

$$P_{tot} = P_0(1+\alpha) = P_0(2 - e^{-kt})$$

1e. If the initial pressure of cyclobutane is 1.00 bar, calculate the time required for the total pressure to be 1.50 bar.
Answer:

$$P_{tot} = P_0(2 - e^{-kt})$$

$$1.50 = 1.00(2 - e^{-kt})$$

$$e^{-2.48\times10^{-4}\ \mathrm{S}^{-1}t} = 0.50$$

$$-2.48 \times 10^{-4}\ \mathrm{s}^{-1} t = \ln(0.50)$$

$$t = -\frac{\ln(0.50)}{2.48\times10^{-4}\ \mathrm{s}^{-1}} = 2.8\times10^{3}\ \mathrm{s}$$