Sheet 2

For the reaction between nitrogen and hydrogen

$$N_2\,(g) + 3\,H_2\,(g) \longrightarrow 2\,NH_3\,(g)$$

the rate of formation of ammonia was measured as 10 mmol dm^{-3} s^{-1}. What was the rate of consumption of hydrogen?

Strategy

Use the stoichiometry of the reaction to determine the rate at which hydrogen is consumed relative to that at which the ammonia is produced.

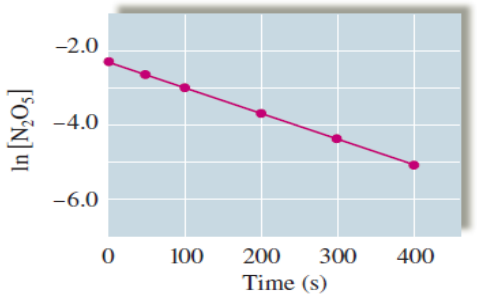
Solution

For every 2 mol of NH_3 (g) produced, 1 mol of N_2 (g) and 3 mol of H_2 (g) are consumed. Thus

$$\begin{aligned}\text{Rate of consumption of hydrogen} &= 3/2 \times \text{ rate of formation of ammonia}\\ &= 1.5 \times 10 \text{ mmol } dm^{-3}s^{-1}\\ &= 15 \text{ mmol } dm^{-3}s^{-1}\end{aligned}$$

The decomposition of N_2O_5 in the gas phase was studied at constant temperature.

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$



$\ln[N_2O_5]$	Time (s)
−2.303	0
−2.649	50
−2.996	100
−3.689	200
−4.382	300
−5.075	400

The following results were collected:

$[N_2O_5]$ (mol/L)	Time (s)
0.1000	0
0.0707	50
0.0500	100
0.0250	200
0.0125	300
0.00625	400

Using these data, verify that the rate law is first order in $[N_2O_5]$, and calculate the value of the rate constant, where the rate $= -\Delta[N_2O_5]/\Delta t$.

Solution

We can verify that the rate law is first order in $[N_2O_5]$ by constructing a plot of $\ln[N_2O_5]$ versus time. The values of $\ln[N_2O_5]$ at various times are given in the table above and the plot of $\ln[N_2O_5]$ versus time is shown in Fig. 12.4. The fact that the plot is a straight line confirms that the reaction is first order in N_2O_5, since it follows the equation $\ln[N_2O_5] = -kt + \ln[N_2O_5]_0$.

Since the reaction is first order, the slope of the line equals $-k$, where

$$\text{Slope} = \frac{\text{change in } y}{\text{change in } x} = \frac{\Delta y}{\Delta x} = \frac{\Delta(\ln[N_2O_5])}{\Delta t}$$

Since the first and last points are exactly on the line, we will use these points to calculate the slope:

$$\text{Slope} = \frac{-5.075 - (-2.303)}{400.\text{ s} - 0\text{ s}} = \frac{-2.772}{400.\text{ s}} = -6.93 \times 10^{-3}\text{ s}^{-1}$$

$$k = -(\text{slope}) = 6.93 \times 10^{-3}\text{ s}^{-1}$$

A certain first-order reaction has a half-life of 20.0 minutes.

a. Calculate the rate constant for this reaction.

Solution

a. Solving Equation (12.3) for k gives

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{20.0\text{ min}} = 3.47 \times 10^{-2}\text{ min}^{-1}$$

Consider the reaction

$$4PH_3(g) \longrightarrow P_4(g) + 6H_2(g)$$

If, in a certain experiment, over a specific time period, 0.0048 mol PH_3 is consumed in a 2.0-L container each second of reaction, what are the rates of production of P_4 and H_2 in this experiment?

Solution

The coefficients in the balanced reaction relate the rate of disappearance of reactants to the rate of production of products. From the balanced reaction, the rate of production of P_4 will be 1/4 the rate of disappearance of PH_3, and the rate of production of H_2 will be 6/4 the rate of disappearance of PH_3. By convention, all rates are given as positive values.

$$\text{Rate} = \frac{-\Delta[PH_3]}{\Delta t} = \frac{(0.0048\ \text{mol}/2.0\ \text{L})}{\text{s}} = 2.4 \times 10^{-3}\ \text{mol/LXs}$$

$$\frac{\Delta[P_4]}{\Delta t} = -\frac{1}{4}\frac{\Delta[PH_3]}{\Delta t} = 2.4 \times 10^{-3}/4 = 6.0 \times 10^{-4}\ \text{mol/LXs}$$

$$\frac{\Delta[H_2]}{\Delta t} = -\frac{6}{4}\frac{\Delta[PH_3]}{\Delta t} = 6(2.4 \times 10^{-3})/4 = 3.6 \times 10^{-3}\ \text{mol/LXs}$$

In the Haber process for the production of ammonia,

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

what is the relationship between the rate of production of ammonia and the rate of consumption of hydrogen?

Solution

$$\frac{\Delta[H_2]}{\Delta t} = 3\frac{\Delta[N_2]}{\Delta t} \text{ and } \frac{\Delta[NH_3]}{\Delta t} = -2\frac{\Delta[N_2]}{\Delta t};\ \text{So,} -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$$

$$\text{or: } \frac{\Delta[NH_3]}{\Delta t} = -\frac{2}{3}\frac{\Delta[H_2]}{\Delta t}$$

Ammonia is produced at a rate equal to 2/3 of the rate of consumption of hydrogen.

At 40°C, $H_2O_2(aq)$ will decompose according to the following reaction:

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

The following data were collected for the concentration of H_2O_2 at various times.

Time (s)	$[H_2O_2]$ (mol/L)
0	1.000
2.16×10^4	0.500
4.32×10^4	0.250

a. Calculate the average rate of decomposition of H_2O_2 between 0 and 2.16×10^4 s. Use this rate to calculate the average rate of production of $O_2(g)$ over the same time period.
b. What are these rates for the time period 2.16×10^4 s to 4.32×10^4 s?

Solution

a. $$\text{average rate} = \frac{-\Delta[H_2O_2]}{\Delta t} = \frac{-(0.500\ M - 1.000\ M)}{(2.16 \times 10^4\ \text{s} - 0)} = 2.31 \times 10^{-5}\ \text{mol/LXs}$$

From the coefficients in the balanced equation:

$$\frac{\Delta[O_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[H_2O_2]}{\Delta t} = 1.16 \times 10^{-5}\ \text{mol/LXs}$$

b. $$\frac{-\Delta[H_2O_2]}{\Delta t} = \frac{-(0.250 - 0.500)\ M}{(4.32 \times 10^4 - 2.16 \times 10^4)\ \text{s}} = 1.16 \times 10^{-5}\ \text{mol/LXs}$$

$$\frac{\Delta[O_2]}{\Delta t} = 1/2\ (1.16 \times 10^{-5}) = 5.80 \times 10^{-6}\ \text{mol/LXs}$$

Notice that as time goes on in a reaction, the average rate decreases.

A certain reaction has the following general form:

$$aA \longrightarrow bB$$

At a particular temperature and $[A]_0 = 2.00 \times 10^{-2}\,M$, concentration versus time data were collected for this reaction, and a plot of ln[A] versus time resulted in a straight line with a slope value of $-2.97 \times 10^{-2}\ \text{min}^{-1}$.

a. Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.

b. Calculate the half-life for this reaction.

c. How much time is required for the concentration of A to decrease to $2.50 \times 10^{-3}\,M$?

Solution

a. Because the ln[A] vs time plot was linear, the reaction is first order in A. The slope of the ln[A] vs. time plot equals !k. Therefore, the rate law, the integrated rate law and the rate constant value are:

$$\text{Rate} = k[A];\ \ \ln[A] = -kt + \ln[A]_o;\ \ k = 2.97 \times 10^{-2}\ \text{min}^{-1}$$

b. The half-life expression for a first-order rate law is:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{k},\ \ t_{1/2} = \frac{0.6931}{2.97 \times 10^{-2}\ \text{min}^{-1}} = 23.3\ \text{min}$$

c. $2.50 \times 10^{-3}\,M$ is 1/8 of the original amount of A present, so the reaction is 87.5% complete. When a first-order reaction is 87.5% complete (or 12.5% remains), the reaction has gone through 3 half-lives:

$$100\% \xrightarrow[t_{1/2}]{} 50.0\% \xrightarrow[t_{1/2}]{} 25\% \xrightarrow[t_{1/2}]{} 12.5\%;\quad t = 3 \times t_{1/2} = 3 \times 23.3\ \text{min} = 69.9\ \text{min}$$

Or we can use the integrated rate law:

$$\ln\left(\frac{[A]}{[A]_o}\right) = -kt,\quad \ln\left(\frac{2.50 \times 10^{-3}\,M}{2.00 \times 10^{-2}\,M}\right) = -(2.97 \times 10^{-2}\ \text{min}^{-1})\,t$$

$$t = \frac{\ln(0.125)}{-2.97 \times 10^{-2}\ \text{min}^{-1}} = 70.0\ \text{min}$$

The radioactive isotope ^{32}P decays by first-order kinetics and has a half-life of 14.3 days. How long does it take for 95.0% of a sample of ^{32}P to decay?

Solution

$$\ln\left(\frac{[A]}{[A]_o}\right) = -kt; \quad k = \frac{\ln 2}{t_{1/2}} = \frac{0.6931}{14.3\ d} = 4.85 \times 10^{-2}\ d^{-1}$$

If $[A]_o = 100.0$, then after 95.0% completion, $[A] = 5.0$.

$$\ln\left(\frac{5.0}{100.0}\right) = !4.85 \times 10^{-2}\ d^{-1} \times t, \quad t = 62 \text{ days}$$

For the reaction A $\rightarrow$ products, successive half-lives are observed to be 10.0, 20.0, and 40.0 min for an experiment in which $[A]_0 = 0.10\ M$. Calculate the concentration of A at the following times.

a. 80.0 min

b. 30.0 min

Solution

Successive half-lives double as concentration is decreased by one-half. This is consistent with second-order reactions so assume the reaction is second order in A.

$$t_{1/2} = \frac{1}{k[A]_o}, \quad k = \frac{1}{t_{1/2}[A]_o} = \frac{1}{10.0\ \text{min}\ (0.10\ M)} = 1.0\ \text{L/molXmin}$$

a. $$\frac{1}{[A]} = kt + \frac{1}{[A]_o} = \frac{1.0\ \text{L}}{\text{mol min}} \times 80.0\ \text{min} + \frac{1}{0.10\ M} = 90.\ M^{-1}, \quad [A] = 1.1 \times 10^{-2}\ M$$

b. 30.0 min = 2 half-lives, so 25% of original A is remaining.

$$[A] = 0.25(0.10\ M) = 0.025\ M$$