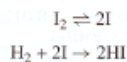


Homework (Apr 17)

9.24 The gas-phase reaction between H_2 and I_2 to form HI involves a two-step mechanism:

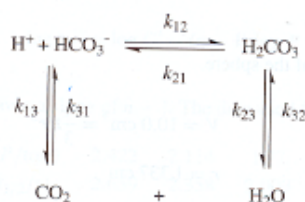


The rate of formation of HI increases with the intensity of visible light. (a) Explain why this fact supports the two-step mechanism given. (*Hint:* The color of I_2 vapor is purple.) (b) Explain why the visible light has no effect on the formation of H atoms.

(a) In this two-step mechanism, the rate determining step is the second one where a hydrogen molecule collides with two iodine atoms. The absorption of visible light by the colored molecular iodine vapor weakens the I_2 bond and increases the number of I atoms present, which in turn increases the reaction rate.

(b) Hydrogen gas is colorless and does not absorb visible light. Ultraviolet light is required to photodissociate H_2 molecules.

9.44 The equilibrium between dissolved CO_2 and carbonic acid can be represented by



Show that

$$-\frac{d[\text{CO}_2]}{dt} = (k_{31} + k_{32})[\text{CO}_2] - \left(k_{13} + \frac{k_{23}}{K}\right)[\text{H}^+][\text{HCO}_3^-]$$

where $K = [\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3]$.

From the equilibrium,

$$\frac{d[\text{CO}_2]}{dt} = k_{13}[\text{H}^+][\text{HCO}_3^-] - k_{31}[\text{CO}_2] + k_{23}[\text{H}_2\text{CO}_3] - k_{32}[\text{CO}_2]$$

Since H_2O is present in a great quantity, the effectively constant concentration, $[\text{H}_2\text{O}]$, is incorporated into the constants k_{31} and k_{32} . Rearranging the expression gives

$$\frac{d[\text{CO}_2]}{dt} = -(k_{31} + k_{32})[\text{CO}_2] + k_{13}[\text{H}^+][\text{HCO}_3^-] + k_{23}[\text{H}_2\text{CO}_3] \quad (9.44.1)$$

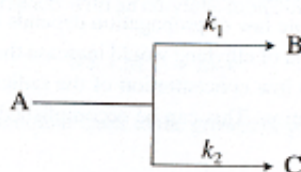
Since H^+ and HCO_3^- are in equilibrium with H_2CO_3 , let

$$\begin{aligned}K &= \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \\ [\text{H}_2\text{CO}_3] &= \frac{[\text{H}^+][\text{HCO}_3^-]}{K}\end{aligned} \quad (9.44.2)$$

Substitute Eq. 9.44.2 into Eq. 9.44.1,

$$\begin{aligned}\frac{d[\text{CO}_2]}{dt} &= -(k_{31} + k_{32})[\text{CO}_2] + k_{13}[\text{H}^+][\text{HCO}_3^-] + k_{23}\frac{[\text{H}^+][\text{HCO}_3^-]}{K} \\ &= -(k_{31} + k_{32})[\text{CO}_2] + \left(k_{13} + \frac{k_{23}}{K}\right)[\text{H}^+][\text{HCO}_3^-] \\ -\frac{d[\text{CO}_2]}{dt} &= (k_{31} + k_{32})[\text{CO}_2] - \left(k_{13} + \frac{k_{23}}{K}\right)[\text{H}^+][\text{HCO}_3^-]\end{aligned}$$

9.51 Consider the following parallel first-order reactions:



- (a) Write the expression for $d[B]/dt$ at time t , given that $[A]_0$ is the concentration of A at $t = 0$.
 (b) What is the ratio of $[B]/[C]$ upon completion of the reactions?

(a) As long as the back reactions can be ignored, $\frac{d[B]}{dt} = k_1[A] = k_1([A]_0 - [B] - [C])$. Likewise, $\frac{d[C]}{dt} = k_2[A] = k_2([A]_0 - [B] - [C])$

(b) Regardless of the importance of the back reactions,

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} + \frac{d[C]}{dt}$$

but if the back reactions can be ignored,

$$-\frac{d[A]}{dt} = (k_1 + k_2)[A]$$

and

$$[A] = [A]_0 e^{-(k_1+k_2)t}$$

From part (a),

$$\begin{aligned} \frac{d[B]}{dt} &= k_1[A] \\ &= k_1[A]_0 e^{-(k_1+k_2)t} \\ d[B] &= k_1[A]_0 e^{-(k_1+k_2)t} dt \\ \int_0^t d[B] &= \int_0^t k_1[A]_0 e^{-(k_1+k_2)t} dt \\ [B]_0^t &= -\frac{k_1[A]_0}{k_1+k_2} e^{-(k_1+k_2)t} \bigg|_0^t \\ [B] &= \frac{k_1[A]_0}{k_1+k_2} [1 - e^{-(k_1+k_2)t}] \end{aligned}$$

since $[B]_0 = 0$. Similarly,

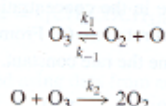
$$[C] = \frac{k_2[A]_0}{k_1+k_2} [1 - e^{-(k_1+k_2)t}]$$

Thus, at any point during the reactions, as long as the back reactions are ignored,

$$\frac{[B]}{[C]} = \frac{k_1}{k_2}$$

At completion, when the reaction reaches equilibrium, the ratio of concentrations is determined by thermodynamic considerations, specifically the difference in Gibbs energy between B and C. At this point, the back reactions can no longer be ignored, as the principle of microscopic reversibility requires that they occur at the same rate as the respective forward reactions.

9.60 Under certain conditions the gas-phase decomposition of ozone is found to be second order in O_3 and inhibited by molecular oxygen. Apply the steady-state approximation to the following mechanism to show that the rate law is consistent with the experimental observations:



State any assumption made in the derivation.

The rate of decomposition of O_3 is

$$\begin{aligned} -\frac{d[O_3]}{dt} &= k_1[O_3] - k_{-1}[O_2][O] + k_2[O][O_3] \\ &= k_1[O_3] + (k_2[O_3] - k_{-1}[O_2])[O] \end{aligned} \quad (9.60.1)$$

Apply the steady state approximation to O:

$$\begin{aligned} \frac{d[O]}{dt} &= k_1[O_3] - k_{-1}[O_2][O] - k_2[O][O_3] = 0 \\ [O] &= \frac{k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]} \end{aligned} \quad (9.60.2)$$

Substitute Eq. 9.60.2 into Eq. 9.60.1:

$$\begin{aligned} -\frac{d[O_3]}{dt} &= k_1[O_3] + (k_2[O_3] - k_{-1}[O_2]) \frac{k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]} \\ &= \frac{k_1 k_{-1}[O_3][O_2] + k_1 k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]} + \frac{k_1 k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]} - \frac{k_1 k_{-1}[O_3][O_2]}{k_{-1}[O_2] + k_2[O_3]} \\ &= \frac{2k_1 k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]} \end{aligned} \quad (9.60.3)$$

If the rate of the second step is assumed to be much slower than the rate of the reverse reaction for the first step, then

$$\begin{aligned} k_2[O][O_3] &\ll k_{-1}[O_2][O] \\ k_2[O_3] &\ll k_{-1}[O_2] \end{aligned}$$

Equation 9.60.3 becomes

$$-\frac{d[O_3]}{dt} = \frac{2k_1 k_2[O_3]^2}{k_{-1}[O_2]}$$

Since the rate for the reaction $2O_3 \rightarrow 3O_2$ is $-\frac{1}{2} \frac{d[O_3]}{dt}$, the rate law predicted by this mechanism is

$$\text{Rate} = -\frac{1}{2} \frac{d[O_3]}{dt} = \frac{k_1 k_2[O_3]^2}{k_{-1}[O_2]}$$

which is consistent with experimental observations.