1.  
   a) From Eq. (6.16), the root-mean-square velocity is
      \[
      (u^2)^{1/2} = (3RT/M)^{1/2} \\
      (3 \cdot 8.314 \text{ J deg}^{-1} \text{ mol}^{-1} \cdot 273 \text{ deg} / 2.016 \times 10^{-3} \text{ kg mol}^{-1})^{1/2} \\
      = 1.838 \times 10^3 \text{ m s}^{-1}
      \]
   
   b) From Eq. (6.14)
      \[
      \overline{U}_\nu = \frac{3}{2} RT \\
      = 1.5 \cdot 8.314 \times 10^{-3} \text{ kJ deg}^{-1} \text{ mol}^{-1} \cdot 273 \text{ deg} \\
      = 3.40 \text{ kJ mol}^{-1}.
      \]
   
   c) According to the ideal gas law, the number of moles \(n\) per unit volume is
      \[
      /V = P/RT.
      \]
      The number of molecules per unit volume is
      \[
      n/V = N_o P /RT
      \]
      where \(N_o\) is Avogadro’s number.
      \[
      N/V = 6.023 \times 10^{23} \text{ mol}^{-1} \cdot 1 \text{ atm} / (82.05 \text{ cm}^3 \text{ atm deg}^{-1} \text{ mol}^{-1} 273 \text{ deg}) \\
      = 2.689 \times 10^{19} \text{ cm}^{-3}.
      \]
   
   d) From Eq. (6.29) \(l = 1/[\sqrt{2\pi(N/V)\sigma^2}]\)
      \[
      N/V = 2.689 \times 10^{19} \text{ cm}^{-3} \\
      \sigma = 2.5 \times 10^{-8} \text{ cm} \\
      l = 1.34 \times 10^{-5} \text{ cm}
      \]
   
   e) From Eq. (6.26)
      \[
      z = 4\sqrt{\pi} \cdot 2.689 \times 10^{35} \text{ m}^{-3} \cdot (2.5 \times 10^{-10} \text{ m})^2 (8.314 \text{ J} \text{ deg}^{-1} \text{ mol}^{-1} \cdot 273 \text{ deg} / 2.016 \times 10^{-3} \text{ kg mol}^{-1})^{1/2} \\
      = 1.264 \times 10^{10} \text{ s}^{-1}.
      \]
   
   f) From Eq. (6.27) \(Z = (N/V)(z/2)\)
      \[
      = 2.689 \times 10^{19} \text{ cm}^{-3} \cdot 1.264 \times 10^{10} \text{ s}^{-1} / 2 \\
      = 1.699 \times 10^{29} \text{ cm}^{-3} \text{ s}^{-1}.
      \]
      \[
      T = \frac{(6.626 \times 10^{-34} \text{ Js})(100 \times 10^6 \text{ s}^{-1})}{(1.5 \times 10^{-5})(1.38 \times 10^{-23} \text{ JK}^{-1})} \\
      T = 320 \text{ K} = 47 \text{ °C}
      \]
4. a) Many methods are described in the text.
   b) Diffusion measurements provide the frictional coefficient of a protein. The radius of a spherical protein can be calculated. Changes in shape can be monitored, sedimentation velocity depends on molecular weight and frictional coefficient. Combination of sedimentation and diffusion gives the molecular weight. Sedimentation equilibrium depends only on molecular weight (for an ideal solution). Electrophoresis depends on net charge on protein and on frictional coefficient. Changes in charge with pH or mutations can be monitored. Gel electrophoresis in sodium dodecylsulfate (SDS) can be calibrated to provide approximate, relative molecular weights.

c) The same molecular properties can be obtained for nucleic acids as for proteins. But for nucleic acids there is one negative charge per nucleotide phosphate. In a denaturing gel, electrophoresis is used to count nucleotides. This leads to a simple method of determining the sequence of a nucleic acid.

1. a) \(-d[I_2]/dt = k[I_2]^a(ket)^b[H^+]^c\)
   Order of reaction with respect to \(I_2\) is 0.
   \[
   \frac{7 \times 10^{-5}}{7 \times 10^{-5}} = \left( \frac{5 \times 10^{-4}}{3 \times 10^{-4}} \right)^a
   
   1 = (1.67)^a \quad a = 0
   
   \]
   Order of reaction with respect to (ket) is 1.
   \[
   \frac{7 \times 10^{-5}}{1.7 \times 10^{-4}} = \left( \frac{0.2}{0.5} \right)^b
   
   0.41 = (0.4)^b \quad b = 1
   
   \]
   Order of reaction with respect to \(H^+\) is 1.
   \[
   \frac{1.7 \times 10^{-4}}{5.4 \times 10^{-4}} = \left( \frac{10^{-2}}{3.2 \times 10^{-2}} \right)^c
   
   0.31 = (0.31)^c \quad c = 1
   
   \]
b) \[-d[I_2]/dt = k[\text{ket}][H^+]\]
\[k = (7 \times 10^{-3})/(0.2 \times 10^{-2}) = 0.035\]
\[k = (1.7 \times 10^{-4})/(0.5 \times 10^{-2}) = 0.034\]
\[k = (5.4 \times 10^{-4})/[(0.5)(3.2 \times 10^{-2})] = 0.034\]
\[k = 0.034 \text{ M}^{-1} \text{s}^{-1}\]

c) The concentration of ketone will stay essentially constant because \(0.5 \gg 10^{-4}\).
\[
d[I_{\text{ket}}]/dt = -d[I_2]/dt = (0.034)(0.5)(10^{-1}) \equiv \Delta[I_{\text{ket}}]/\Delta t
\]
\[\Delta t = \frac{10^{-4}}{(0.034)(0.5)(10^{-1})} = 0.059 \text{ s}\]
Doubling concentration of ket or \(H^+\) will double rate; doubling \(I_2\) will produce no effect.
It is impossible to synthesize \(10^{-1}\) M \(I_{\text{ket}}\), because the \(10^{-3}\) M \(I_2\) limits the maximum concentration that can be formed.

d) To be consistent with the velocity expression
\[v = k[\text{ket}][H^+]\]
the step involving \(I_2\) should not be rate-determining

\[
\text{ketone} + H^+ \rightarrow H^+ \cdot \text{ketone} \quad \text{(slow)}
\]
\[H^+ \cdot \text{ketone} + I_2 \rightarrow \text{iodoketone} + H^+ \quad \text{(fast)}
\]

5. a) \[d[C]/dt = k[A]^a[B]^b\]
\[4 \times 10^{-3} = \left(\frac{2}{1}\right)^a\]
\[a = 2\]
\[4 = 2^a\]
\[b = 0\]
\[10^{-3} = \left(\frac{2}{1}\right)^b\]

b) Order of reaction with respect to \([A]\) is 2
\[10^{-3} = \left(\frac{2}{1}\right)^b\]
\[b = 0\]

Order of reaction with respect to \([B]\) is 0

c) \[d[C]/dt = k[A]^2\]
d) \[k = (10^{-3} \text{ M s}^{-1})/(1 \text{ M})^2 = 10^{-3} \text{ M}^{-1} \text{ s}^{-1}\]
e) \[A + A \xrightarrow{k_1} A_2 \quad \text{(slow)}\]
\[A_2 + B \xrightarrow{k_2} C + D + A \quad \text{(fast)}\]
First reaction is rate determining. Rate of formation of \(C\) is essentially equal to rate of formation of \(A_2\).
\[d[C]/dt = d[A_2]/dt = k_1[A]^2\]
6. \[ \nu = -d[S]/dt = k \]
\[ -d[S] = kdt \]
\[ \int d[S] = [S] - [S]_0 = -k \int dt = -kt - 0 \]
\[ 1/2[S]_0 - [S]_0 = -kt_{1/2} \]
\[ t_{1/2} = [S]_0 / 2k \]

7. a) \[ d[D]/dt = k_1[B][C] \]
\[ d[B]/dt = k_1[A] - k_2[B] - k_3[B][C] \leq 0 \]
\[ k_1[A] = (k_2 + k_3[C])B \]
\[ [B] = k_1[A]/(k_2 + k_3[C]) \]
\[ d[D]/dt = k_3k_1[A][C]/(k_2 + k_3[C]) \]

b) \[ d[D]/dt = k[AB][C] \]
\[ K = [AB]/[A][B] \]
\[ d[D]/dt = kK[A][B][C] \]

10. a) \[ [A] = [A]_0 e^{-kt} \]
\[ 0.10 = e^{-k(1 \text{ hr})} \]
\[ k = \frac{-\ln 0.10}{1 \text{ hr}} = 2.30 \text{ hr}^{-1} \]
At 2 hr \[ [A]/[A]_0 = e^{-k(2 \text{ hr})} = e^{-4.60} = 0.010 \]

b) \[ 1/[A] - 1/[A]_0 = kt \]
\[ 1/(0.10[A]_0) - 1/[A]_0 = k(1 \text{ hr}) \]
\[ k = 9/[A]_0 \text{ hr}^{-1} \]
At 2 hr, \[ 1/[A] = 1/[A]_0 + k(2 \text{ hr}) \]
\[ = 1/[A]_0 + (9/[A]_0)(2) = 19/[A]_0 \]
\[ [A]/[A]_0 = 1/19 = 0.0526 \]

c) \[ [A]_0 - [A] = kt \]
\[ [A]_0 - 0.1[A]_0 = k(1 \text{ hr}) \]
\[ k = 0.9[A]_0 \text{ hr}^{-1} \]
At 2 hr, \[ [A] = [A]_0 - k(2 \text{ hr}) = [A]_0 - 1.8[A]_0 = -0.8[A]_0 \]
The concentration will reach zero before 2 hr elapses. For all zero-order reactions the rate law must eventually change as concentrations approach zero.

d) \[-d[A]/dt = k[A][B]^{1/2}\]

but \([A]_0 = [B]_0\) and \([A] = [B]\) at all times

\[-d[A]/dt = k[A]^{1/2}\]

\[
\frac{1}{1/2} \left( \frac{1}{[A]_0^{1/2}} - \frac{1}{[A]_0} \right) = kt \quad \text{from Eq. (7.25)}
\]

\[
2\left[ \frac{1}{(0.1[A]_0^{1/2})^{1/2}} - \frac{1}{[A]_0^{1/2}} \right] = 4.325 \sqrt{[A]_0^{1/2}} = k(1 \text{ hr})
\]

\[
k = 4.325[A]_0^{1/2} \text{ hr}^{-1}
\]

At 2 hr, \(2 \left( [A]^{1/2} - [A]_0^{1/2} \right) = 4.325[A]_0^{1/2}(2)\)

\[
[A]^{1/2} = (4.325 + 1)[A]_0^{1/2} = 5.325[A]_0^{1/2}
\]

\[
\left( \frac{[A]}{[A]_0} \right)^{1/2} = \frac{1}{5.325}
\]

\[
[A]/[A]_0^{1/2} = (1/5.325)^2 = 0.0353
\]

Additional Problems:

\[
\text{Rate (CH}_4\text{)} = \sqrt{\frac{32T}{M_{CH}_4}}
\]

\[
\text{Rate (Ar)} = \sqrt{\frac{M_{Ar} A_0}{M_{CH}_4 \text{ CH}_4}}
\]

\[
\text{Rate (CH}_4\text{)} = \text{Rate (Ar)} \sqrt{\frac{39.95 g/\text{min}}{16.048 g/\text{min}}}
\]

\[
= 0.46166 \frac{L}{\text{min}} \times \frac{60 \text{ min}}{1 \text{ hr}} = 27.9 \frac{L}{\text{hr}}
\]
Additional Problems:

1. Rate reaction: \( \frac{d[CO_2]}{dt} = \frac{1}{2} \frac{d[CO_2]}{dt} = \frac{1}{3} \frac{d[CO_2]}{dt} \)

   \[
   \frac{d[CO_2]}{dt} = -\frac{3}{2} \frac{d[CO_2]}{dt} = -\frac{3}{2} \left(-7.2 \times 10^{-4} \text{ M s}^{-1}\right) \]

   \[= +1.08 \times 10^{-3} \text{ M s}^{-1} \]

2. 3rd order overall

3. \( \text{M s}^{-1} = k \text{ MM}^2 \)

   \[k = \frac{M \text{ s}^{-1}}{M^3} = \frac{-2}{-1} \]

4. \( t_{1/2} = \frac{\ln 2}{k} \quad k = \frac{\ln 2}{t_{1/2}} = 1.77 \times 10^{-5} \text{ s}^{-1} \)

   \[
   [A] = [A]_0 e^{-kt} \]

   \[= 0.88 \text{ M Exp} \left[-1.77 \times 10^{-5} \text{ s}^{-1} \times 2.20 \text{ day} \times \frac{24 \text{ hr}}{1 \text{ day}} \times \frac{3600 \text{ s}}{1 \text{ hr}} \right] \]

   \[= 0.0304 \text{ M} \]
\[ k = Ae^{-\frac{E_a}{RT}} \]

\[ \ln k = \ln A - \frac{E_a}{RT} \]

\[ \ln \frac{k_2}{k_1} = \ln \frac{\frac{k_2}{k_1}}{\frac{k_2}{k_1}} = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]

\[ E_a = -\frac{\ln \frac{k_2}{k_1}}{\left( \frac{1}{T_2} - \frac{1}{T_1} \right)} = -\frac{\ln \left( \frac{5.79 \times 10^{-4}}{346 \times 10^{-4}} \right)}{\frac{1}{318} - \frac{1}{298}} \]

\[ = -\frac{4.23 \text{ J mol}^{-1} \text{ K}^{-1}}{-2.11 \times 10^{-4} \text{ K}^{-1}} \]

\[ = 2.03 \times 10^4 \text{ J mol}^{-1} \]

\[ = 20.3 \text{ kJ mol}^{-1} \]