

CHEM 402—Physical Chemistry
Chapter 24 Homework Solutions

mathematics package, or graphically by plotting the right-hand side vs. the (constant) left-hand side and finding the value of λ at which the two lines cross. The reorganization energy turns out to be:

$$\lambda = 1.9 \times 10^{-19} \text{ J} \text{ or about } 1.2 \text{ eV}.$$

E24.17(a) For the same donor and acceptor at different distances, eqn 24.83 applies:

$$\ln k_{\text{et}}/\text{s}^{-1} = -\beta r + \text{constant}.$$

The slope of a plot of k_{et} versus r is $-\beta$. The slope of a line defined by two points is

$$\text{slope} = \frac{\Delta y}{\Delta x} = \frac{(\ln k_{\text{et},2}/\text{s}) - (\ln k_{\text{et},1}/\text{s})}{r_2 - r_1} = -\beta = \frac{\ln 4.51 \times 10^4 - \ln 2.02 \times 10^5}{(1.23 - 1.11) \text{ nm}},$$

$$\beta = 12 \text{ nm}^{-1}.$$

Solutions to problems

Solutions to numerical problems

P24.2 Draw up the following table as the basis of an Arrhenius plot

| T/K | 600 | 700 | 800 | 1000 |
|--|-------------------|-------------------|-------------------|-------------------|
| $10^3 \text{ K}/T$ | 1.67 | 1.43 | 1.25 | 1.00 |
| $k/(\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ | 4.6×10^2 | 9.7×10^3 | 1.3×10^5 | 3.1×10^6 |
| $\ln(k/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ | 6.13 | 9.18 | 11.8 | 14.9 |

The points are plotted in Figure 24.1.

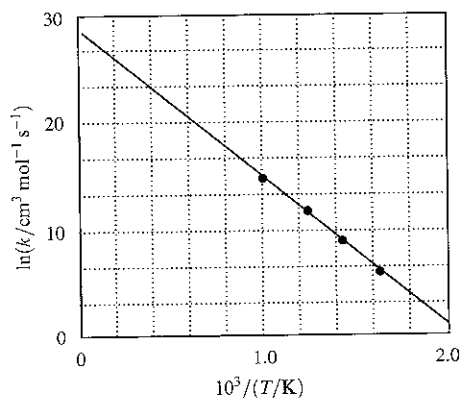


Figure 24.1

The least-squares intercept is at 28.3, which implies that

$$A/(\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = e^{28.3} = 2.0 \times 10^{12}$$

From $A = N_A \sigma^* \left(\frac{8kT}{\pi \mu} \right)^{1/2}$ [Exercise 24.13(a)]

$$\begin{aligned} \sigma^* &= \frac{A_{\text{exptl}}}{N_A (8kT/\pi \mu)^{1/2}} \quad \text{with } \mu = \frac{1}{2} m(\text{NO}_2) \\ &= \left(\frac{A_{\text{exptl}}}{4N_A} \right) \left(\frac{\pi m}{kT} \right)^{1/2} = \left(\frac{2.0 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}{(4) \times (6.022 \times 10^{23} \text{ mol}^{-1})} \right) \\ &\quad \times \left(\frac{(\pi) \times (46 \text{ u}) \times (1.6605 \times 10^{-27} \text{ kg u}^{-1})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (750 \text{ K})} \right)^{1/2} \\ &= 4.0 \times 10^{-21} \text{ m}^2 \quad \text{or} \quad \boxed{4.0 \times 10^{-3} \text{ nm}^2} \end{aligned}$$

$$P = \frac{\sigma^*}{\sigma} = \frac{4.0 \times 10^{-3} \text{ nm}^2}{0.60 \text{ nm}^2} = \boxed{0.007}$$

P24.4 Draw up the following table for an Arrhenius Plot

| | | | | | |
|-------------------------|--------|--------|--------|--------|--------|
| $\theta/^\circ\text{C}$ | -24.82 | -20.73 | -17.02 | -13.00 | -8.95 |
| T/K | 248.33 | 252.42 | 256.13 | 260.15 | 264.20 |
| $10^3/(T/\text{K})$ | 4.027 | 3.962 | 3.904 | 3.844 | 3.785 |
| $\ln(k/\text{s}^{-1})$ | -9.01 | -8.37 | -7.73 | -7.07 | -6.55 |

The points are plotted in Figure 24.2.

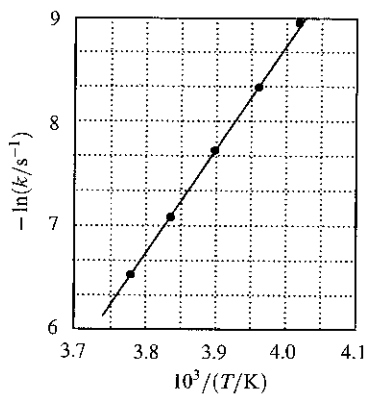


Figure 24.2

A least-squares fit of the data yields the intercept $+32.6$ at $1/T = 0$ and slope $-10.33 \times 10^3 \text{ K}$. The former implies that $\ln(A/\text{s}^{-1}) = 32.6$, and hence that $A = 1.4 \times 10^{14} \text{ s}^{-1}$. The slope yields $E_a/R = 10.33 \times 10^3 \text{ K}$, and hence $E_a = \boxed{85.9 \text{ kJ mol}^{-1}}$

In solution $\Delta^\ddagger H = E_a - RT$, so at -20°C

$$\begin{aligned}\Delta^\ddagger H &= (85.9 \text{ kJ mol}^{-1}) - (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (253 \text{ K}) \\ &= \boxed{83.8 \text{ kJ mol}^{-1}}\end{aligned}$$

We assume that the reaction is first-order for which, by analogy to Section 24.4

$$K^\ddagger = K = \frac{kT}{hv} \bar{K}^\ddagger$$

$$\text{and } k_1 = k^\ddagger K^\ddagger = v \times \frac{kT}{hv} \times \bar{K}^\ddagger$$

$$\text{with } \Delta^\ddagger G = -RT \ln \bar{K}^\ddagger$$

$$\text{Therefore, } k_1 = A e^{-E_a/RT} = \frac{kT}{h} e^{-\Delta^\ddagger G/RT} = \frac{kT}{h} e^{\Delta^\ddagger S/R} e^{-\Delta^\ddagger H/RT}$$

and hence we can identify $\Delta^\ddagger S$ by writing

$$k_1 = \frac{kT}{h} e^{\Delta^\ddagger S/R} e^{-E_a/RT} = A e^{-E_a/RT}$$

and hence obtain

$$\begin{aligned}\Delta^\ddagger S &= R \left[\ln \left(\frac{hA}{kT} \right) - 1 \right] \\ &= 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times \left[\ln \left(\frac{(6.626 \times 10^{-34} \text{ J s}) \times (1.4 \times 10^{14} \text{ s}^{-1})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (253 \text{ K})} \right) - 1 \right] \\ &= \boxed{+19.1 \text{ J K}^{-1} \text{ mol}^{-1}}\end{aligned}$$

$$\text{Therefore, } \Delta^\ddagger G = \Delta^\ddagger H - T \Delta^\ddagger S = 83.8 \text{ kJ mol}^{-1} - 253 \text{ K} \times 19.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= \boxed{+79.0 \text{ kJ mol}^{-1}}$$

P24.6 Figure 24.3 shows that $\log k$ is proportional to the ionic strength for neutral molecules.

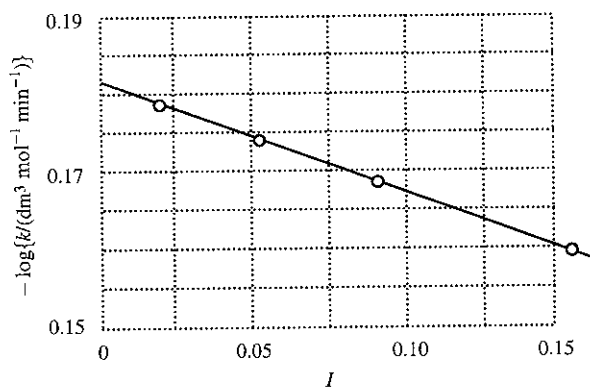


Figure 24.3

The product of charges works out to be 0.9, nearly 1, interpretable in terms of a complex of two univalent ions of the same sign

P24.10 $A + A \rightarrow A_2 \quad \Delta v = -1$

$$\begin{aligned} \Delta^\ddagger S &= R \left(\ln \left[\frac{A}{(kT/h) \times (RT/p^\ominus)} \right] + 2 \right) \quad [24.63] \\ &= -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &\quad \times \left[\ln \left[\frac{4.07 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} (m^3/10^3 \text{ dm}^3)}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (300 \text{ K})^2 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})} \right. \right. \\ &\quad \left. \left. \frac{1}{(6.626 \times 10^{-34} \text{ J s}) \times (1.013 \times 10^5 \text{ Pa})} \right] + 2 \right] \\ &= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times [\ln(2.631 \times 10^{-9}) + 2] \end{aligned}$$

$$\Delta^\ddagger S = -148 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \Delta^\ddagger H &= E_a - 2RT = 65.43 \text{ kJ mol}^{-1} - 2 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K}) \\ &\quad \times \left(\frac{10^{-3} \text{ kJ}}{\text{J}} \right) \quad [24.60, 24.61] \end{aligned}$$

$$\Delta^\ddagger H = 60.44 \text{ kJ mol}^{-1}$$

$$\Delta^\ddagger H = \Delta^\ddagger U + \Delta^\ddagger(pV)$$

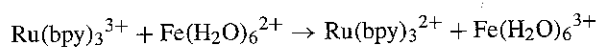
$$\begin{aligned} \Delta^\ddagger U &= \Delta^\ddagger H - \Delta^\ddagger(pV) = \Delta^\ddagger H - \Delta v RT \\ &= (60.44 \text{ kJ mol}^{-1}) - (-1) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K}) \times \left(\frac{10^{-3} \text{ kJ}}{\text{J}} \right) \end{aligned}$$

$$\Delta^\ddagger U = 62.9 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta^\ddagger G &= \Delta^\ddagger H - T \Delta^\ddagger S = 60.44 \text{ kJ mol}^{-1} - (300 \text{ K}) \times (-148 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &\quad \times \left(\frac{10^{-3} \text{ kJ}}{\text{J}} \right) \quad [24.59] \end{aligned}$$

$$\Delta^\ddagger G = 104.8 \text{ kJ mol}^{-1}$$

P24.12 Estimate the bimolecular rate constant k_{12} for the reaction



by using the approximate Marcus cross-relation:

$$k_{12} \approx (k_{11}k_{22}K)^{1/2}$$

$$24.9 \quad (a) \quad \frac{d[\text{F}_2\text{O}]}{dt} = -k_1[\text{F}_2\text{O}]^2 - k_2[\text{F}][\text{F}_2\text{O}], \quad (1)$$

$$\frac{d[\text{F}]}{dt} = k_1[\text{F}_2\text{O}]^2 - k_2[\text{F}][\text{F}_2\text{O}] + 2k_3[\text{OF}]^2 - 2k_4[\text{F}]^2[\text{F}_2\text{O}], \quad (2)$$

$$\frac{d[\text{OF}]}{dt} = k_1[\text{F}_2\text{O}]^2 + k_2[\text{F}][\text{F}_2\text{O}] - 2k_3[\text{OF}]^2. \quad (3)$$

Applying the steady-state approximation to both [F] and [OF] and adding the resulting equations gives

$$\begin{array}{rcl} k_1[\text{F}_2\text{O}]^2 - k_2[\text{F}]_{\text{SS}}[\text{F}_2\text{O}] + 2k_3[\text{OF}]_{\text{SS}}^2 & -2k_4[\text{F}]_{\text{SS}}^2[\text{F}_2\text{O}] & = 0 \\ k_1[\text{F}_2\text{O}]^2 + k_2[\text{F}]_{\text{SS}}[\text{F}_2\text{O}] - 2k_3[\text{OF}]_{\text{SS}}^2 & & = 0 \end{array}$$

$$2k_1[\text{F}_2\text{O}]^2 \qquad \qquad \qquad -2k_4[\text{F}]_{\text{SS}}^2[\text{F}_2\text{O}] = 0$$

Solving for [F]_{SS} gives

$$[\text{F}]_{\text{SS}} = \left(\frac{k_1}{k_4} [\text{F}_2\text{O}] \right)^{1/2}.$$

Substituting (4) into (1)

$$\frac{d[\text{F}_2\text{O}]}{dt} = k_1[\text{F}_2\text{O}]^2 - k_2 \left(\frac{k_1}{k_4} \right)^{1/2} [\text{F}_2\text{O}]^{3/2}$$

or

$$\boxed{-\frac{d[\text{F}_2\text{O}]}{dt} = k_1[\text{F}_2\text{O}]^2 + k_2 \left(\frac{k_1}{k_4} \right)^{1/2} [\text{F}_2\text{O}]^{3/2}.$$

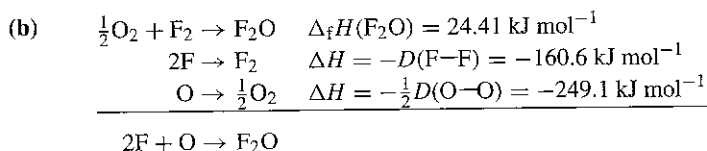
Comparison with the experimental rate law reveals that they are consistent when we make the following identifications.

$$k = k_1 = 7.8 \times 10^{13} e^{-E_1/RT} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

$$E_1 = (19350 \text{ K})R = 160.9 \text{ kJ mol}^{-1},$$

$$k' = k_2 \left(\frac{k_1}{k_4} \right)^{1/2} = 2.3 \times 10^{10} e^{-E'/RT} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

$$E' = (16910 \text{ K})R = 140.6 \text{ kJ mol}^{-1}.$$



$$\begin{aligned}\Delta H(\text{FO-F}) + \Delta H(\text{O-F}) &= -\left[\Delta_f H(\text{F}_2\text{O}) - D(\text{F-F}) - \frac{1}{2}D(\text{O-O})\right] \\ &= -(24.41 - 160.6 - 249.1) \text{ kJ mol}^{-1} \\ &= 385.3 \text{ kJ mol}^{-1}.\end{aligned}$$

We estimate that $\Delta H(\text{FO-F}) \approx E_1 = 160.9 \text{ kJ mol}^{-1}$.

Then

$$\begin{aligned}\Delta H(\text{O-F}) &= 385.3 \text{ kJ mol}^{-1} - \Delta H(\text{FO-F}) \\ &\approx (385.3 - 160.9) \text{ kJ mol}^{-1}.\end{aligned}$$

$$\Delta H(\text{O-F}) \approx 224.4 \text{ kJ mol}^{-1}.$$

In order to determine the activation energy of reaction (2) we assume that each rate is expressed in Arrhenius form, then

$$\ln k' = \ln k_2 + \frac{1}{2} \ln k_1 - \frac{1}{2} \ln k_4$$

or

$$\ln A' - \frac{E'}{RT} = \ln A_2 - \frac{E_2}{RT} + \frac{1}{2} \ln A_1 - \frac{1}{2} \frac{E_1}{RT} - \frac{1}{2} \ln A_4 + \frac{1}{2} \frac{E_4}{RT}.$$

Differentiating with respect to T , we obtain

$$E' = E_2 + \frac{1}{2}E_1 - \frac{1}{2}E_4 = 140.6 \text{ kJ mol}^{-1}$$

or

$$\begin{aligned}E_2 - \frac{1}{2}E_4 &= E' - \frac{1}{2}E_1 = (140.6 - 80.4) \text{ kJ mol}^{-1} \\ &= 60.2 \text{ kJ mol}^{-1}.\end{aligned}$$

E_4 is expected to be small since reaction (4) is termolecular, so we set $E_4 \approx 0$; then

$$E_2 \approx 60 \text{ kJ mol}^{-1}.$$

P24.11 Linear regression analysis of $\ln(\text{rate constant})$ against $1/T$ yields the following results:

$$\ln(k/22.4 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}) = C + B/T$$

where $C = 34.36$, standard deviation = 0.36,

$B = -23227 \text{ K}$, standard deviation = 252 K,

$R = 0.99976$ [good fit].

$$\ln(k'/22.4 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}) = C_2 + B_2/T$$

where $C' = 28.30$, standard deviation = 0.84,
 $B' = -21065 \text{ K}$, standard deviation = 582 K,
 $R = \boxed{0.99848}$ [good fit].

The regression parameters can be used in the calculation of the pre-exponential factor (A) and the activation energy (E_a) using $\ln k = \ln A - E_a/RT$.

$$\ln A = C + \ln(22.4) = 37.47,$$

$$A = 1.87 \times 10^{16} \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1} = \boxed{3.12 \times 10^{14} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}.$$

$$E_a = -RB = -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (-23227 \text{ K}) \times \left(\frac{10^{-3} \text{ kJ}}{\text{J}}\right) \\ = \boxed{193 \text{ kJ mol}^{-1}}.$$

$$\ln A' = C' + \ln(22.4) = 31.41,$$

$$A' = 4.37 \times 10^{13} \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1} = \boxed{7.29 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}.$$

$$E'_a = -RB' = -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (-21065 \text{ K}) \times \left(\frac{10^{-3} \text{ kJ}}{\text{J}}\right) \\ = \boxed{175 \text{ kJ mol}^{-1}}.$$

To summarize

| | $A/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ | $E_a/(\text{kJ mol}^{-1})$ |
|------|---|----------------------------|
| k | $3.12 \times 10^{14} (= A)$ | 193 |
| k' | $7.29 \times 10^{11} (= A')$ | 175 |

Both sets of data, k and k' , fit the Arrhenius equation very well and hence are consistent with the collision theory of bimolecular gas-phase reactions which provides an equation 24.19 compatible with the Arrhenius equation. The numerical values for k' and A may be compared to the results of Exercise 24.7(a) and are in rough agreement at 647 K, as is the value of E_a .

Solutions to theoretical problems

P24.13

$$[J]^* = k \int_0^t [J]e^{-kt} dt + [J]e^{-kt} [24.40],$$

$$\frac{\partial [J]^*}{\partial t} = k[J]e^{-kt} + \frac{\partial [J]}{\partial t} e^{-kt} - k[J]e^{-kt} = \left(\frac{\partial [J]}{\partial t}\right) e^{-kt},$$

$$\frac{\partial^2 [J]^*}{\partial x^2} = k \int_0^t \left(\frac{\partial^2 [J]}{\partial x^2}\right) e^{-kt} dt + \left(\frac{\partial^2 [J]}{\partial x^2}\right) e^{-kt}.$$

(2) For collisions between nonlinear molecules

$$q_A^\ominus = (q_A^R)^3 (q_A^V)^{3N-6} (q_A^T) \approx (10^{1.5})^3 \times (1) \times (10^{26}) \approx 3 \times 10^{30},$$

$$q_B^\ominus = (q_B^R)^3 (q_B^V)^{3N'-6} (q_B^T) \approx 3 \times 10^{30},$$

$$q_C^\ominus = (q_C^R)^3 (q_C^V)^{3(N+N')-6} (q_C^T) \approx 3 \times 10^{30}.$$

$$k_2(\text{molecules}) \propto \frac{3 \times 10^{30}}{1 \times 10^{61}} = 3 \times 10^{-31}.$$

$$\text{Therefore } k_2(\text{atoms})/k_2(\text{molecules}) \approx \frac{10^{-23}}{3 \times 10^{-31}} \approx \boxed{3 \times 10^7}.$$

Solutions to applications

P24.23 Collision theory gives for a rate constant with no energy barrier

$$k = P\sigma \left(\frac{8kT}{\pi\mu} \right)^{1/2} N_A \quad \text{so} \quad P = \frac{k}{\sigma N_A} \left(\frac{\pi\mu}{8kT} \right)^{1/2}.$$

$$P = \frac{k/(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}) \times (10^{-3} \text{m}^3 \text{dm}^{-3})}{(\sigma/\text{nm}^2) \times (10^{-9} \text{m})^2 \times (6.022 \times 10^{23} \text{mol}^{-1})} \\ \times \left(\frac{\pi \times (\mu/\text{u}) \times (1.66 \times 10^{-27} \text{kg})}{8 \times (1.381 \times 10^{-23} \text{J K}^{-1}) \times (298 \text{K})} \right)^{1/2} \\ = \frac{(6.61 \times 10^{-13})k/(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})}{(\sigma/\text{nm}^2) \times (\mu/\text{u})^{1/2}}.$$

The collision cross-section is

$$\sigma_{AB} = \pi d_{AB}^2 \quad \text{where } d_{AB} = \frac{1}{2}(d_A + d_B) = \frac{\sigma_A^{1/2} + \sigma_B^{1/2}}{2\pi^{1/2}} \quad \text{so} \quad \sigma_{AB} = \frac{(\sigma_A^{1/2} + \sigma_B^{1/2})^2}{4}.$$

The collision cross-section for O_2 is listed in the *Data section*. We would not be far wrong if we took that of the ethyl radical to equal that of ethene; similarly, we will take that of cyclohexyl to equal that of benzene. For O_2 with ethyl

$$\sigma = \frac{(0.40^{1/2} + 0.64^{1/2})^2}{4} \text{ nm}^2 = 0.51 \text{ nm}^2,$$

$$\mu = \frac{m_{\text{O}} m_{\text{e}}}{m_{\text{O}} + m_{\text{e}}} = \frac{(32.0 \text{ u}) \times (29.1 \text{ u})}{(32.0 + 29.1) \text{ u}} = 15.2 \text{ u},$$

$$\text{so } P = \frac{(6.61 \times 10^{-13}) \times (4.7 \times 10^9)}{(0.51) \times (15.2)^{1/2}} = \boxed{1.6 \times 10^{-3}}$$

For O₂ with cyclohexyl

$$\sigma = \frac{(0.40^{1/2} + 0.88^{1/2})^2}{4} \text{ nm}^2 = 0.62 \text{ nm}^2,$$

$$\mu = \frac{m_{\text{O}}m_{\text{C}}}{m_{\text{O}} + m_{\text{C}}} = \frac{(32.0 \text{ u}) \times (77.1 \text{ u})}{(32.0 + 77.1) \text{ u}} = 22.6 \text{ u},$$

$$\text{so } P = \frac{(6.61 \times 10^{-13}) \times (8.4 \times 10^9)}{(0.62) \times (22.6)^{1/2}} = \boxed{1.8 \times 10^{-3}}.$$

P24.25 Equation 24.69 may be written in the form:

$z_{\text{A}}^2 = \frac{1}{2A} \frac{\log(k_2/k_2^0)}{I^{1/2}}$ where we have used $z_{\text{A}} = z_{\text{B}}$ for the cationic protein. This equation suggests that z_{A} can be determined through analysis that uses the mean value of $(\log(k_2/k_2^0))/I^{1/2}$ for several experiments over a range of various ionic strengths.

$$z_{\text{A}} = \sqrt{\frac{1}{2A} \text{mean} \left\{ \frac{\log(k_2/k_2^0)}{I^{1/2}} \right\}}.$$

We draw up a table that contains data rows needed for the computation.

| | | | | | | |
|-----------------------|--------|--------|--------|--------|--------|--------|
| I | 0.0100 | 0.0150 | 0.0200 | 0.0250 | 0.0300 | 0.0350 |
| k/k^0 | 8.10 | 13.30 | 20.50 | 27.80 | 38.10 | 52.00 |
| $\log(k/k^0)/I^{0.5}$ | 9.08 | 9.18 | 9.28 | 9.13 | 9.13 | 9.17 |

$$\text{mean} \{ \log(k/k^0)/I^{0.5} \} = 9.17,$$

$$z_{\text{A}} = \sqrt{\frac{1}{2A} \text{mean} \left\{ \frac{\log(k_2/k_2^0)}{I^{1/2}} \right\}} = \sqrt{\frac{9.16}{2(0.509)}} = \boxed{+3.0}$$

where we have used the positive root because the protein is cationic.

P24.27 Does eqn 24.83,

$$\ln k_{\text{et}} = -\beta r + \text{constant},$$

apply to these data? Draw the following table.

| r/nm | $k_{\text{et}}/\text{s}^{-1}$ | $\ln k_{\text{et}}/\text{s}^{-1}$ |
|---------------|-------------------------------|-----------------------------------|
| 0.48 | 1.58×10^{12} | 28.1 |
| 0.95 | 3.98×10^9 | 22.1 |
| 0.96 | 1.00×10^9 | 20.7 |
| 1.23 | 1.58×10^8 | 18.9 |
| 1.35 | 3.98×10^7 | 17.5 |
| 2.24 | 6.31×10^1 | 4.14 |