

1. 60 pts

- (a) A Carnot cycle engine has the  $PV$  cycle drawn below. Explain how we could adjust one parameter to make the engine more efficient, and show on the graph how the cycle would be different. **Solution:** The efficiency is equal to  $(T_{\text{hot}} - T_{\text{cold}})/T_{\text{hot}}$ , so the greater the difference in temperature, the greater the efficiency. Lowering  $T_{\text{cold}}$  has a bigger effect than raising  $T_{\text{hot}}$  by the same amount.
- (b) In a Monte Carlo simulation at 300 K, determine the **range of values** of the random number  $y$  (where  $0 < y < 1$ ) such that we will keep a new trial state that has potential energy  $200 \text{ cm}^{-1}$  greater than the current state. **Solution:**

$$y < e^{-\Delta U/(k_B T)} = e^{-200/(0.6950 \cdot 300)} = 0.383 \quad \boxed{y < 0.383.}$$

- (c) Find the vapor pressure of  $\text{Br}_2$  at 298 K given that  $\Delta_{\text{vap}}H^\ominus = 29.96 \text{ kJ mol}^{-1}$  and  $T_b = 331.9 \text{ K}$ . **Solution:**

$$\ln P(\text{bar}) = \frac{\Delta_{\text{vap}}H}{R} \left[ \frac{1}{T_b} - \frac{1}{T} \right] = \frac{(29.96 \text{ kJ mol}^{-1})(10^3 \text{ J/kJ})}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left[ \frac{1}{331.9 \text{ K}} - \frac{1}{298 \text{ K}} \right] = -1.235$$

$$P = e^{-1/235} = \boxed{0.291 \text{ bar}}$$

- (d) The vapor pressure of  $\text{ClO}$  above a  $0.100 \text{ M}$  aqueous solution of  $\text{ClO}$  is  $0.14 \text{ bar}$  at  $298 \text{ K}$ . Find the Henry's law coefficient  $k_X$  at this temperature. **Solution:**

$$X_B = \frac{[\text{B}]}{[\text{H}_2\text{O}][\text{B}]} = \frac{0.100 \text{ mol}}{(0.100 + 55.56) \text{ mol}} = 1.80 \cdot 10^{-3}$$

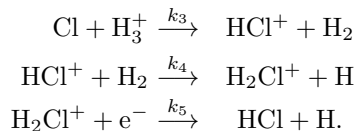
$$k_X = \frac{P_B}{X_B} = \frac{0.14 \text{ bar}}{1.80 \cdot 10^{-3}} = \boxed{78 \text{ bar.}}$$

- (e) A calorimeter with a bath heat capacity of  $8370 \text{ J K}^{-1}$  measures a temperature increase of  $0.100 \text{ K}$  in the bath upon the folding of a  $1.63 \cdot 10^{-3} \text{ mol}$  sample of cellular lysozyme. What is  $\Delta_{\text{rxn}}H^\ominus$  for the folding of this protein? **Solution:**

$$n\Delta_{\text{rxn}}H^\ominus = -q_{\text{bath}} = -C \Delta T$$

$$\Delta_{\text{rxn}}H^\ominus = -\frac{C \Delta T}{n} = -\frac{(8370 \text{ J K}^{-1})(0.100 \text{ K})}{1.63 \cdot 10^{-3} \text{ mol}} = -5.13 \cdot 10^5 \text{ J mol}^{-1} = \boxed{-513 \text{ kJ mol}^{-1}.}$$

- (f) Write the rate law (*not* the integrated rate law) for the  $\text{H}_2\text{Cl}^+$  intermediate in the reaction mechanism

**Solution:**

$$\frac{d[\text{H}_2\text{Cl}^+]}{dt} = k_4[\text{HCl}^+][\text{H}_2] - k_5[\text{H}_2\text{Cl}^+][\text{e}^-].$$

2.  $3.60 \text{ g}$  of liquid water are placed inside a chamber with a piston at  $298 \text{ K}$ . The initial volume of the liquid is negligible. The water completely evaporates, and the piston is pushed out to allow the vapor to expand reversibly and isothermally against a pressure of  $0.0100 \text{ bar}$ . Calculate  $w$  and  $\Delta S$  for the process in SI units. **Solution:**

- (a) The work is done to expand the gas against the 0.100 bar external pressure. The phase transition—the vaporization itself—requires only heat, not work.

$$n = \frac{m}{M} = \frac{3.60 \text{ g}}{18.0 \text{ g mol}^{-1}} = 0.200 \text{ mol}$$

$$V_2 = \frac{nRT}{P} = \frac{(0.200 \text{ mol})(0.083145 \text{ bar L K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{0.100 \text{ bar}} = 49.6 \text{ L}$$

$$w = -P_{\min} \Delta V \approx -P_{\min} V_2 = -(0.100 \text{ bar})(49.6 \text{ L})(10^2 \text{ J bar}^{-1} \text{ L}^{-1}) = \boxed{496 \text{ J}}$$

- (b) The entropy change involves a phase transition at non-standard temperature and pressure, and so we consider that process as a series of several steps: (1) raise the pressure of the liquid to 1.00 bar to reach the standard state; (2) heat the liquid to the normal boiling point at 373 K; (3) vaporize the water under standard conditions; (4) cool the vapor back to 298 K; (5) reduce the pressure back to 0.100 bar.

$$\Delta S = \Delta_1 S + \Delta_2 S + \Delta_3 S + \Delta_4 S + \Delta_5 S$$

$$\Delta_1 S \approx 0 \text{ for an incompressible liquid}$$

$$\Delta_2 S = nC_{Pm}(l) \ln \frac{T_2}{T_1} = (0.200 \text{ mol})(75.291 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{373}{298} = 3.380 \text{ J K}^{-1}$$

$$\Delta_3 S = n\Delta_{\text{vap}} S^\ominus = n \frac{\Delta_{\text{vap}} H^\ominus}{T} = \frac{40.65 \cdot 10^3 \text{ J mol}^{-1}}{373 \text{ K}} = 109.0 \text{ J K}^{-1}$$

$$\Delta_4 S = nC_{Pm}(g) \ln \frac{T_2}{T_1} = (0.200 \text{ mol})(33.577 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{298}{373} = -1.507 \text{ J K}^{-1}$$

$$\Delta_5 S = nR \ln \frac{V_2}{V_1} = nR \ln \frac{P_1}{P_2} = (0.200 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{1.00}{0.100} = 3.829 \text{ J K}^{-1}$$

$$\Delta S = (0 + 3.380 + 109.0 - 1.507 + 3.829) \text{ J K}^{-1} = \boxed{115 \text{ J K}^{-1}}$$

3. Recall that the  $\text{p}K_a$  of an acid HA is  $-\log_{10} K_a$  where  $K_a$  is the equilibrium constant for the dissociation of HA into  $\text{H}^+$  and  $\text{A}^-$ . The  $\text{p}K_a$  of *o*-aminobenzoic acid decreases linearly from 6.35 at 283 K to 5.50 at 323 K. What are  $\Delta_{\text{rxn}} H$  and  $\Delta_{\text{rxn}} S$  for the dissociation?

$$\text{p}K_a = -\log_{10} K_a = -\log_{10} e^{-\Delta G^\ominus / (RT)} = \frac{\Delta G^\ominus}{RT} \log_{10}(e)$$

$$= \left( \frac{\Delta H^\ominus}{RT} - \frac{\Delta S^\ominus}{R} \right) \log_{10}(e)$$

Treating  $\Delta H^\ominus$  and  $\Delta S^\ominus$  is temperature-independent:

$$\Delta S^\ominus = \frac{\Delta H^\ominus(T_1)}{T_1} - \frac{R \text{p}K_a(T_1)}{\log_{10}(e)} = \frac{\Delta H^\ominus(T_2)}{T_2} - \frac{R \text{p}K_a(T_2)}{\log_{10}(e)}$$

$$\Delta H^\ominus = \frac{\frac{R}{\log_{10}(e)} (\text{p}K_a(T_1) - \text{p}K_a(T_2))}{\frac{1}{T_1} - \frac{1}{T_2}}$$

$$= \frac{\frac{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}{0.4343} (6.35 - 5.50)}{\frac{1}{283 \text{ K}} - \frac{1}{323 \text{ K}}} = \boxed{37.2 \text{ kJ mol}^{-1}}$$

$$\Delta S^\ominus = \frac{\Delta H^\ominus(T_1)}{T_1} - \frac{R \text{p}K_a(T_1)}{\log_{10}(e)} = \frac{37.2 \cdot 10^3 \text{ J mol}^{-1}}{283 \text{ K}} - \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(6.35)}{0.4343} = \boxed{9.88 \text{ J K}^{-1} \text{ mol}^{-1}}$$

4. The phase diagram below describes mixtures of copper and zinc, which form brass. (Although the horizontal axis is percent weight, for copper and zinc this is roughly equal to mole fraction of Zn.)

- (a) The common form of brass is a “duplex” alloy that combines the  $\alpha$  and  $\beta$  forms of the solid. What is the melting point for duplex brass? **Solution:**  $905^\circ\text{C}$ .
- (b) What is the approximate molecular formula of the low-temperature  $\beta$ -alloy? **Solution:**  $\text{CuZn}$ .
- (c) If have a sample of 90% Zn at equilibrium at  $400^\circ\text{C}$ , and we increase the temperature to  $500^\circ\text{C}$ , what change would we observe in the mixture? **Solution:** The  $\eta$  form of the solid would melt, while the  $\epsilon$  form would remain solid.
- (d) As we heat the  $\beta$  form of the solid from  $500^\circ\text{C}$  to  $800^\circ\text{C}$ , it becomes stable over a wider range of composition (% Zn). The opposite is true for the  $\gamma$  phase. How does this suggest  $\beta$  brass differs from  $\gamma$  brass? **Solution:** As  $T$  approaches the melting point, the  $\beta$  form is more stable than competing crystal structures of similar composition, whereas the  $\gamma$  form becomes less stable. That suggests that the  $\gamma$  form is more dense than the  $\beta$ , so that the vibrations of the atoms at higher temperatures are more constrained in the  $\gamma$  than the  $\beta$ .
5. In the reaction  $\text{CCl}_4 + \text{Br} \rightarrow \text{CBrCl}_3 + \text{Cl}$ , the Br atom can attack the  $\text{CCl}_4$  at any of four equivalent sites. If we calculate  $\Delta_1 H^\ddagger$ ,  $\Delta_1 S^\ddagger$ , and  $k_1$  for a reaction at one of those sites, what values should we find for  $\Delta_4 H^\ddagger$ ,  $\Delta_4 S^\ddagger$ , and  $k_4$ —the parameters when we consider all four reaction sites? In other words, find  $\Delta_4 H^\ddagger$ ,  $\Delta_4 S^\ddagger$ , and  $k_4$  as functions of  $\Delta_1 H^\ddagger$ ,  $\Delta_1 S^\ddagger$ , and  $k_1$ .

(a)  $\Delta_4 H^\ddagger = \Delta_1 H^\ddagger$

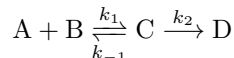
(b)

$$\Delta_1 S^\ddagger = k_B (\ln \Omega^\ddagger - \ln \Omega_1) = k_B \ln \frac{\Omega^\ddagger}{\Omega_1}$$

$$\Delta_4 S^\ddagger = k_B (\ln(4\Omega^\ddagger) - \ln \Omega_1) = k_B \ln \frac{4\Omega^\ddagger}{\Omega_1} = k_B \ln 4 + \Delta_1 S^\ddagger$$

(c)  $k_4 = 4k_1$

6. For the reaction



Eq. 14.23 gives this expression for the concentration of A in the the steady-state approximation:

$$[\text{A}]' = [\text{A}]_0 \left(1 - \frac{[\text{A}]_0}{[\text{B}]_0}\right) \left\{ \exp \left[ -([\text{B}]_0 - [\text{A}]_0) \left(1 - \frac{k_{-1}}{k_{-1} + k_2}\right) k_1 t \right] - \frac{[\text{A}]_0}{[\text{B}]_0} \right\}^{-1}.$$

- (a) Simplify this equation for the case that  $[\text{A}]_0 = [\text{B}]_0$ . **Solution:** Let  $[\text{B}]_0 - [\text{A}]_0 = x$  approach zero:

$$\begin{aligned} [\text{A}]' &= [\text{A}]_0 \left(1 - \frac{[\text{A}]_0}{[\text{B}]_0}\right) \left\{ \exp \left[ -([\text{B}]_0 - [\text{A}]_0) \left(1 - \frac{k_{-1}}{k_{-1} + k_2}\right) k_1 t \right] - \frac{[\text{A}]_0}{[\text{B}]_0} \right\}^{-1} \\ &= \frac{[\text{A}]_0}{[\text{B}]_0} ([\text{B}]_0 - [\text{A}]_0) \left\{ \exp \left[ -([\text{B}]_0 - [\text{A}]_0) \left(1 - \frac{k_{-1}}{k_{-1} + k_2}\right) k_1 t \right] - \frac{[\text{A}]_0}{[\text{B}]_0} \right\}^{-1} \\ &= \frac{[\text{A}]_0}{[\text{B}]_0} x \left\{ \exp \left[ -x \left(1 - \frac{k_{-1}}{k_{-1} + k_2}\right) k_1 t \right] - \frac{[\text{A}]_0}{[\text{B}]_0} \right\}^{-1} \end{aligned}$$

Let  $e^{-ax} = 1 - ax$  as  $x$  approaches 0:

$$\begin{aligned}
\lim_{x \rightarrow 0} [A]' &= \frac{[A]_0}{[B]_0} x \left\{ \left[ 1 - x \left( 1 - \frac{k_{-1}}{k_{-1} + k_2} \right) k_1 t \right] - \frac{[A]_0}{[B]_0} \right\}^{-1} \\
&= \frac{[A]_0}{[B]_0} x \left\{ 1 - x \left( 1 - \frac{k_{-1}}{k_{-1} + k_2} k_1 t \right) - \frac{[A]_0}{[B]_0} \right\}^{-1} \\
&= \frac{[A]_0}{[B]_0} x \left\{ 1 - \frac{[A]_0}{[B]_0} - x \left( 1 - \frac{k_{-1}}{k_{-1} + k_2} k_1 t \right) \right\}^{-1} \\
&= \frac{[A]_0}{[B]_0} x \left\{ \frac{1}{[B]_0} x - x \left( 1 - \frac{k_{-1}}{k_{-1} + k_2} k_1 t \right) \right\}^{-1} \\
&= \frac{[A]_0}{[B]_0} \left\{ \frac{1}{[B]_0} - \left( 1 - \frac{k_{-1}}{k_{-1} + k_2} k_1 t \right) \right\}^{-1} \\
&= [A]_0 \left\{ 1 - [B]_0 \left( 1 - \frac{k_{-1}}{k_{-1} + k_2} k_1 t \right) \right\}^{-1} \\
&= [A]_0 \left\{ 1 - [B]_0 \frac{k_{-1} + k_2 - k_{-1} k_1 t}{k_{-1} + k_2} \right\}^{-1} \\
&= [A]_0 \left\{ 1 - \frac{k_2 [B]_0}{k_{-1} + k_2} k_1 t \right\}^{-1} \\
&= [A]_0 \left\{ \frac{k_{-1} + k_2 - k_2 [B]_0 k_1 t}{k_{-1} + k_2} \right\}^{-1} \\
&= \frac{[A]_0 (k_{-1} + k_2)}{k_{-1} + k_2 - k_2 [B]_0 k_1 t} \\
&= \frac{[A]_0 (k_{-1} + k_2)}{k_{-1} + k_2 - k_2 [A]_0 k_1 t}.
\end{aligned}$$

(b) Show that your solution still gives the correct result in the limit that  $t = 0$ .

$$\lim_{t \rightarrow 0} [A]' = \frac{[A]_0 (k_{-1} + k_2)}{k_{-1} + k_2} [A]_0.$$

(c) Show that your solution still gives the correct result in the limit that  $k_2 \gg k_{-1}$ .

$$\lim_{k_2 \gg k_{-1}} [A]' = \frac{[A]_0 (k_2)}{k_2 - k_2 [A]_0 k_1 t} = \frac{[A]_0}{1 - [A]_0 k_1 t}$$

This is the correct equation for the concentration of A in the reaction  $2A \xrightarrow{k_1} \text{products}$ .