Chemistry 236
Spectrophotometry Study Problems -- Answers

1. To derive Eq. (7), start with the exact expression (2) and set $[M] \approx [M]_0$. Then solve for x (= $[I_2\text{•}M]$). Next substitute for x from the Beer-Lambert law, $x = A_x/(\varepsilon_x \ell)$, invert the resulting equation, and rearrange terms to obtain (7). The version in Question 3 is then obtained by multiplying through by $[M]_0$. In general you would not get identical results analyzing the data these two different ways, because they effectively weight the data differently.

2. 0.30 M in y & 0.64 M in z.

3. (a) $I/I_0 = 10^{-A} = 0.2205$.

   (b) $A = \varepsilon\, c\, \ell \rightarrow c = 6.7 \times 10^{-5}$ M.

   (c) $[I_2]_{eq} = [I_2]_0 - [I_2\text{•}M]_{eq}$.

   $[I_2]_0 = 3.00/5.00 \times 0.00155$ M $= 9.3 \times 10^{-4}$ M $\rightarrow$

   $[I_2]_{eq} = 8.63 \times 10^{-4}$ M.

   Similarly, $[M]_0 = 0.132$ M and $[M]_{eq} = 0.1319$ M.

   (d) $K_c = \dfrac{[I_2\text{•}M]_{eq}}{[M]_{eq}\,[I_2]_{eq}} = 0.588$.

4. Use the van't Hoff equation (*e.g.*, Eq. 6.39 in Levine, or p. 460 in ONF) to obtain ΔH°. Then use $RT \ln K = -\Delta G^\circ$ (see, *e.g.*, p. 457 in ONF) to calculate ΔG° for either of the two Ts. Finally use the relation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ for a process at constant T (see, *e.g.*, p. 454 in ONF) to obtain ΔS°.

   $\Delta H^\circ = -14.0$ kJ/mol; $\Delta G^\circ = 0.0$ at 22.0°C $\Delta S^\circ = -47.5$ J mol^{-1} K^{-1}.

   Methods like those used in Prob. 4 of Expt. 2 yield $s(\Delta H^\circ) = 3.0_2$ kJ/mol, so $\Delta H^\circ = -14.0 \pm 3.0$ kJ/mol. The error in ΔG° is negligible compared with that in ΔH°, so the error in $T\Delta S^\circ$ is equal to that in ΔH°. This gives a slightly T-dependent error in ΔS°. The average for the two Ts is 9.94 J mol^{-1} K^{-1} (which agrees with the result from a more sophisticated approach). Hence, $\Delta S^\circ = -48 \pm 10$ J mol^{-1} K^{-1}.

5. (a) $T = 0.1169$; $\varepsilon = 809._7$ L mol^{-1} cm^{-1}.

   (b) At equilibrium, $[I_2] = 5.28_6 \times 10^{-4}$ M, $[M] = 3.92_3 \times 10^{-4}$ M, & $[I_2\text{•}M] = 1.90_8 \times 10^{-4}$ M. Thus, $K_c = 920$ L/mol.