Answers to Exercise 7.3 Calculating Free Energy for Reactions Under Nonstandard Conditions

1.
(a)
$$CS_{2(g)} + 4H_{2(g)} \rightarrow CH_{4(g)} + 2H_2S_{(g)}$$

(b) $\Delta_r G^\circ = \sum \Delta_f G^\circ(products) - \sum \Delta_f G^\circ(reactants)$
 $\Delta_r G^\circ = [\Delta_f G^\circ(CH_{4(g)}) + 2\Delta_f G^\circ(H_2S_{(g)})] - [\Delta_f G^\circ(CS_{2(g)}) + 4\Delta_f G^\circ(H_{2(g)})]$
 $\Delta_r G^\circ = [(-50.72\frac{kJ}{mol}) + 2(-33.56\frac{kJ}{mol})] - [(67.1\frac{kJ}{mol}) + 4(0\frac{kJ}{mol})]$
 $\Delta_r G^\circ = -184.9\frac{kJ}{mol}$

The answer is significant to one decimal place, but use all digits $\left(-184.94 \frac{kJ}{mol}\right)$ when you take this value to part (c).

(c) Step 1: Convert temperature to Kelvin

$$T = 25 \,^{\circ}\text{C} = 298.15 \, K$$

Step 2: Determine activities for all reactants and products

$$a_{CS_{2(g)}} = \frac{0.15 \ bar}{1 \ bar} = 0.15 \qquad a_{CH_{4(g)}} = \frac{1.25 \ bar}{1 \ bar} = 1.25 \\ a_{H_{2(g)}} = \frac{1.65 \ bar}{1 \ bar} = 1.65 \qquad a_{H_{2}S_{(g)}} = \frac{0.35 \ bar}{1 \ bar} = 0.35$$

Step 3: Calculate reaction quotient

$$Q = \frac{\left(a_{CH_{4(g)}}\right)\left(a_{H_{2}S_{(g)}}\right)^{2}}{\left(a_{CS_{2(g)}}\right)\left(a_{H_{2(g)}}\right)^{4}} = \frac{(1.25)(0.35)^{2}}{(0.15)(1.65)^{4}} = 0.14$$

Step 4: Calculate free energy change for reaction under nonstandard conditions $\Delta_r G = \Delta_r G^\circ + RT lnQ$

$$\Delta_r G = \left(-184.9 \frac{kJ}{mol}\right) + \left(8.314\ 462 \frac{J}{mol \cdot K}\right) \left(\frac{1\ kJ}{1000\ J}\right) (298.15\ K) ln(0.14)$$

$$\Delta_r G = \left(-184.9 \frac{kJ}{mol}\right) + \left(-4.91 \frac{kJ}{mol}\right)$$

$$\Delta_r G = -189.9 \frac{kJ}{mol}$$

Step 5: Check your work

Does your answer seem reasonable? Are sig. fig. correct?

2.

(a) **Step 1: Write a balanced chemical equation for the reaction**

This was provided in the question.

 $2 SO_{2(g)} + O_{2(g)} \rightarrow 2 SO_{3(g)}$

Step 2: Convert temperature to Kelvin (if necessary)

 $T = 25 \,^{\circ}\text{C} = 298.15 \, K$

Step 3: Calculate the standard free energy change for the reaction

$$\Delta_{r}G^{\circ} = \sum \Delta_{f}G^{\circ}(products) - \sum \Delta_{f}G^{\circ}(reactants)$$

$$\Delta_{r}G^{\circ} = 2 \Delta_{f}G^{\circ}(SO_{3(g)}) - \left[2 \Delta_{f}G^{\circ}(SO_{2(g)}) + \Delta_{f}G^{\circ}(O_{2(g)})\right]$$

$$\Delta_{r}G^{\circ} = 2\left(-371.1\frac{kJ}{mol}\right) - \left[2\left(-300.2\frac{kJ}{mol}\right) + \left(0\frac{kJ}{mol}\right)\right]$$

$$\Delta_{r}G^{\circ} = -141.8\frac{kJ}{mol}$$

Step 4: Determine activities for all reactants and products

$$a_{SO_{2}(g)} = \frac{0.48 \text{ bar}}{1 \text{ bar}} = 0.48$$

$$a_{SO_{3}(g)} = \frac{0.72 \text{ bar}}{1 \text{ bar}} = 0.72$$

$$a_{O_{2}(g)} = \frac{0.18 \text{ bar}}{1 \text{ bar}} = 0.18$$

Step 5: Calculate reaction quotient

$$Q = \frac{\left(a_{SO_{3(g)}}\right)^{2}}{\left(a_{SO_{2(g)}}\right)^{2} \left(a_{O_{2(g)}}\right)} = \frac{(0.72)^{2}}{(0.48)^{2} (0.18)} = 12.5$$
 but only 2 sig. fig.

Step 6: Calculate free energy change for reaction under nonstandard conditions

$$\begin{aligned} \Delta_r G &= \Delta_r G^{\circ} + RT lnQ \\ \Delta_r G &= \left(-141.8 \frac{kJ}{mol} \right) + \left(8.314\ 462 \frac{J}{mol \cdot K} \right) \left(\frac{1\ kJ}{1000\ J} \right) (298.15\ K) ln(12.5) \\ \Delta_r G &= \left(-141.8 \frac{kJ}{mol} \right) + \left(6.26 \frac{kJ}{mol} \right) \\ \Delta_r G &= -135.5 \frac{kJ}{mol} \end{aligned}$$

Step 7: Check your work

Does your answer seem reasonable? Are sig. fig. correct?

(b) A catalyst has no effect on the position of equilibrium. The catalyst's role is to speed up both the forward and reverse reactions. It may, therefore help the system reach a state of equilibrium more quickly.