1.

$$\mathrm{C(s, graph) + CO_2(g) \rightleftharpoons 2\,CO\,(g)} \quad \Delta H^\circ = 172.5\,\frac{\mathrm{kJ}}{\mathrm{mol}},\ \Delta S^\circ = 175.9\,\frac{\mathrm{J}}{\mathrm{mol{\cdot}K}}$$

At 298 K, a reaction flask is set up with 100 g of C(s, graphite), $P_{CO_2} = 75$ bar, and $P_{CO} = 2$ bar.

Fill in the blanks with $>, <, =$, or X for cannot be determined

(a) Q ___$>$___ K

(b) ΔG_T ___$>$___ 0

(c) K ___$<$___ 1

$$Q = \frac{(P_{CO})^2}{P_{CO_2}} = \frac{2^2}{75} = 0.053$$

$$\begin{aligned} K &= \exp\left(\frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}\right) \\ &= \exp\left(\frac{175.9\,\frac{\mathrm{J}}{\mathrm{mol\cdot K}}}{8.314\,\frac{\mathrm{J}}{\mathrm{mol\cdot K}}} - \frac{172{,}500\,\frac{\mathrm{J}}{\mathrm{mol}}}{8.314\,\frac{\mathrm{J}}{\mathrm{mol\cdot K}} \cdot 298\,\mathrm{K}}\right) \\ &= 1.24 \times 10^{-21} \end{aligned}$$

2.

$$\mathrm{2\,Cl_2(g) + 2\,H_2O\,(g) \rightleftharpoons 4\,HCl\,(g) + O_2(g)} \quad K_{753\,\mathrm{K}} = 0.0613$$

(a) A constant-pressure vessel is assembled at 753 K with initial concentrations:

$$[\mathrm{Cl_2}] = 7.94 \times 10^{-3}\,\mathrm{mol} \qquad [\mathrm{H_2O}] = 6.35 \times 10^{-3}\,\mathrm{mol}$$
$$[\mathrm{HCl}] = 9.53 \times 10^{-3}\,\mathrm{mol} \qquad [\mathrm{O_2}] = 3.17 \times 10^{-3}\,\mathrm{mol}$$

When equilibrium is reached, does the volume increase, decrease, stay the same, or cannot be determined?

$$\begin{aligned} Q_c &= \frac{[\mathrm{HCl}]^4[\mathrm{O_2}]}{[\mathrm{Cl_2}]^2[\mathrm{H_2O}]^2} \\ &= \frac{(9.53 \times 10^{-3})^4 \cdot (3.17 \times 10^{-3})}{(7.94 \times 10^{-3})^2 \cdot (6.35 \times 10^{-3})^2} = 0.0103 \end{aligned}$$

$$Q = \left(\frac{c^\circ RT}{P^\circ}\right)^{\Delta n} Q_c$$

$$\Delta n = 5 - 4 = 1$$

$$Q = 0.0103 \cdot \frac{1\,\frac{\mathrm{mol}}{\mathrm{L}} \cdot 0.08314\,\frac{\mathrm{L\cdot bar}}{\mathrm{mol\cdot K}} \cdot 753\,\mathrm{K}}{1\,\mathrm{bar}} = 0.645$$

$$Q > K \implies \text{reaction shifts left, fewer gas molecules, volume decreases}$$

(b) Suppose the vessel was assembled under standard conditions instead, with the same concentrations and allowed to reach equilibrium. Compare the reaction quotient to the equilibrium constant to determine what happens to the volume. $\Delta H^\circ_{\text{rxn}} = 114{,}400\,\text{J}$.

$$\begin{aligned}
\ln\frac{K_2}{K_1} &= -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\\
&= -\frac{114{,}400\,\frac{\text{J}}{\text{mol}}}{8.314\,\frac{\text{J}}{\text{mol}\cdot\text{K}}}\left(\frac{1}{298\,\text{K}}-\frac{1}{753\,\text{K}}\right)\\
&= -27.90\\
K_2 &= 0.0613\cdot e^{-27.90} = 5.11\times10^{-14}\\
\Delta n &= 5-4 = 1
\end{aligned}$$

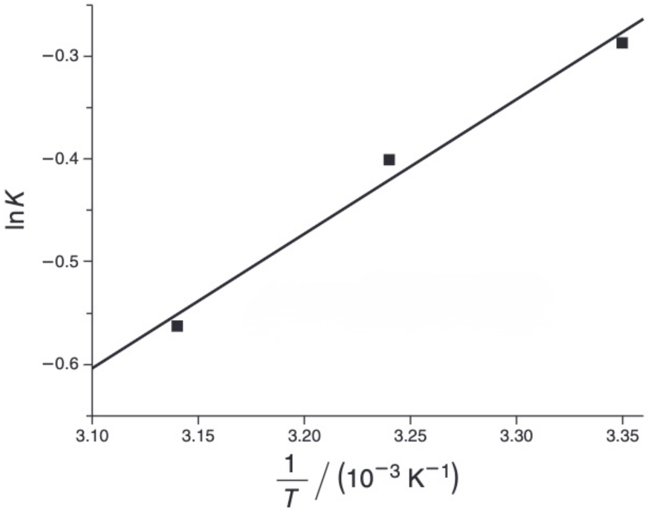
$$Q = Q_c\cdot\left(\frac{c^\circ RT}{P^\circ}\right)^{\Delta n} = 0.0103\cdot\frac{(1\,\frac{\text{mol}}{\text{L}})(0.08314\,\frac{\text{L}\cdot\text{bar}}{\text{mol}\cdot\text{K}})(298\,\text{K})}{1\,\text{bar}} = 0.255$$

$$Q > K_{298} \implies \text{reaction shifts left, fewer moles of gas, volume decreases}$$

3. (**J. Chem. Educ. 2009**, *86*, 1330.)

$$\text{I}_2 + \text{mes} \rightleftharpoons [\text{I}_2\text{—mes}]$$

Equilibrium constants for the complexation reaction were determined over a range of temperatures. A plot of $\ln K$ (where K is the equilibrium constant) vs. $1/T$ was compiled from the data.. The data points form a line with a slope of 1299 Kelvin and a y-intercept of -4.69. Determine ΔH°, ΔS°, ΔG°, and determine the conditions under which the reaction is spontaneous (i.e., at low vs. high temperatures).



Van't Hoff equation: $\ln K = -\frac{\Delta H^\circ}{R}\frac{1}{T} + \frac{\Delta S^\circ}{R}$

$$\begin{aligned}
m &= -\frac{\Delta H^\circ}{R} \implies \Delta H^\circ = -m\cdot R\\
\Delta H^\circ &= -1{,}299\,\text{K}\cdot 8.314\,\frac{\text{J}}{\text{mol}\cdot\text{K}} = \boxed{-10{,}800\,\frac{\text{J}}{\text{mol}}}\\
b &= \frac{\Delta S^\circ}{R} \implies \Delta S^\circ = b\cdot R\\
\Delta S^\circ &= -4.69\cdot 8.314\,\frac{\text{J}}{\text{mol}\cdot\text{K}} = \boxed{-38.9\,\frac{\text{J}}{\text{mol}\cdot\text{K}}}\\
\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ\\
&= -10{,}800\,\frac{\text{J}}{\text{mol}} - 298\,\text{K}\cdot\left(-38.9\,\frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\\
&= \boxed{822\,\frac{\text{J}}{\text{mol}}}
\end{aligned}$$

Spontaneity: $\Delta H < 0 \qquad \Delta S < 0 \implies$ Low T

Homework Problem 24

1. For the chemical equilibrium:

$$2\,NO_2(g) \rightleftharpoons N_2O_4(g)$$

first determine K_c at standard conditions. Experimentally, it is measured at K_c is 215. Was this experiment conducted above, at, or below standard conditions?

	ΔH_f° ($\frac{kJ}{mol}$)	S_m° ($\frac{J}{mol\cdot K}$)
$NO_2(g)$	33.18 $\frac{kJ}{mol}$	240.06 $\frac{J}{mol\cdot K}$
$N_2O_4(g)$	9.16 $\frac{kJ}{mol}$	304.29 $\frac{J}{mol\cdot K}$