1) Solid NH_4NO_3 is placed in a beaker containing water at 25 °C. When the solid has completely dissolved, the temperature of the solution is 23.5 °C.

(a) Was the process exothermic or endothermic?
(b) Did the entropy of the system increase?

a. Endothermic. The surroundings (water) releases heat into the system, thereby decreasing the temperature of the surroundings.
b. Yes, the compound went from a solid to an aqueous state, or from a more ordered to a less ordered state.

2) Predict whether each of the following processes results in an increase in entropy in the system. (Define reactants and products as the system.)

a) Atmospheric water vapor condenses as dew (liquid water) at 0 °C and 1 atm pressure.

Decrease in entropy of system, goes from gas to liquid state…less disordered

b) An exothermic reaction of $Al(s)$ and $Br_2(\ell)$ forms $Al_2Br_6(s)$

Decrease in entropy of system, goes from liquid to solid state with more bonds…less disordered.

c) The endothermic decomposition of solid $CaCO_3$ at 800 °C to produce an equilibrium mixture containing solid $CaCO_3$, solid CaO, and gaseous CO_2

Increase in entropy of system, gas is formed…more disordered.

d) One mol of AgCl(s) decomposes, forming 1.0 mole of Ag(s) and 0.5 mol $Cl_2(g)$.

Increase in entropy of system, gas is formed…more disordered.

3) Calculate the standard entropy change for the formation of 1.0 mol of the following compounds from the elements at 25 °C.

a) HCl(g)

b) $Ca(OH)_2(s)$

a.)

$\Delta S°_{rxn} = \Sigma S°_{products} - \Sigma S°_{reactants}$

The chemical equation at standard state is: $1/2H_2(g) + 1/2Cl_2(g) \rightarrow HCl(g)$

$\Delta S°_{rxn} = [186.9] - [0.5*130.7 + 0.5*223.1]$

$\Delta S°_{rxn} = 10$ J/(K*mol)

b.)

$\Delta S°_{rxn} = \Sigma S°_{products} - \Sigma S°_{reactants}$

The chemical equation at standard state is: $Ca(s) + O_2(g) + H_2(g) \rightarrow Ca(OH)_2(s)$

$\Delta S°_{rxn} = [83.4] - [1*41.59+ 1*205.07 + 1*130.7]$

$\Delta S°_{rxn} = -294$ J/(K*mol)

4) Is the reaction $Si(s) + 2 Cl_2(g) \rightarrow SiCl_4(g)$ spontaneous under standard conditions at 298.15 K? Answer this question by calculating ΔS°(system), ΔS°(surroundings), and ΔS°(universe). (Define reactants and products as the system.)

$\Delta S°_{system} = \Sigma S°_{products} - \Sigma S°_{reactants}$

$\Delta S°_{system} = [330.86] - [1*18.8 + 2*223.1]$

$\Delta S°_{system} = -134.14$ J/(K*mol)

$\Delta S°_{surroundings} = \Delta H°_{reaction} / T$

Figure out unknown value: $\Delta H°_{reaction}$

$\Delta H°_{reaction} = \Sigma \Delta H°_{products} - \Sigma \Delta H°_{reactants}$

$\Delta H°_{reaction} = [–662.75] - [1*0 + 2*0]$

$\Delta H°_{reaction} = –662.75$ kJ/mol

$\Delta S°_{surroundings} = -662.75$ kJ/mol / 298.15 K

$\Delta S°_{surroundings} = -2.223$ kJ/(mol*K) = 2223 J/(mol*K)

$\Delta S°_{universe} = \Delta S°_{system} + \Delta S°_{surroundings}$

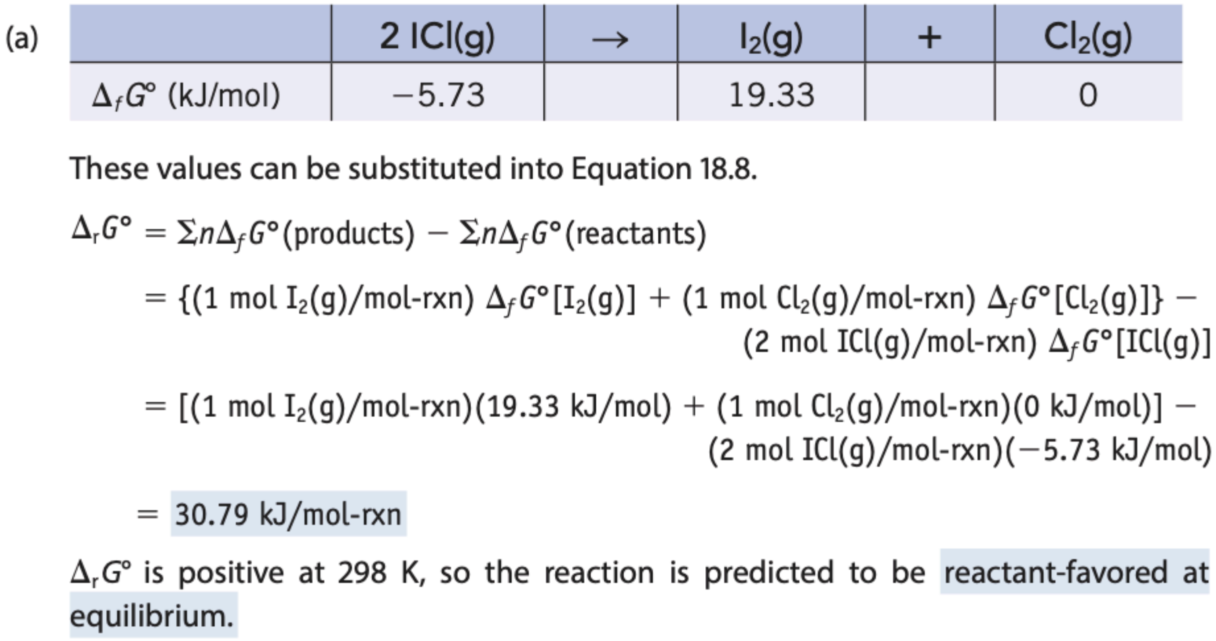
$\Delta S°_{universe} = -134.14$ J/(K*mol) + 2223 J/(mol*K)

$\Delta S°_{universe} = 2088.9$ J/(mol*K)

$\Delta S°_{universe} > 0$, therefore, the reaction is spontaneous under standard conditions

5) Gaseous iodine monochloride can be decomposed into iodine and chlorine gases according to the following chemical equation 2 ICl(g) → $I_2(g) + Cl_2(g)$

a) Calculate $\Delta_r G°$ for this reaction at 298 K using values for the standard free energies of formation of the products and reactant. Is this reaction reactant-favored or product-favored at equilibrium?



(a)

	2 ICl(g)	→	$I_2(g)$	+	$Cl_2(g)$
$\Delta_f G°$ (kJ/mol)	−5.73		19.33		0

These values can be substituted into Equation 18.8.

$$\Delta_r G° = \Sigma n \Delta_f G°(\text{products}) - \Sigma n \Delta_f G°(\text{reactants})$$

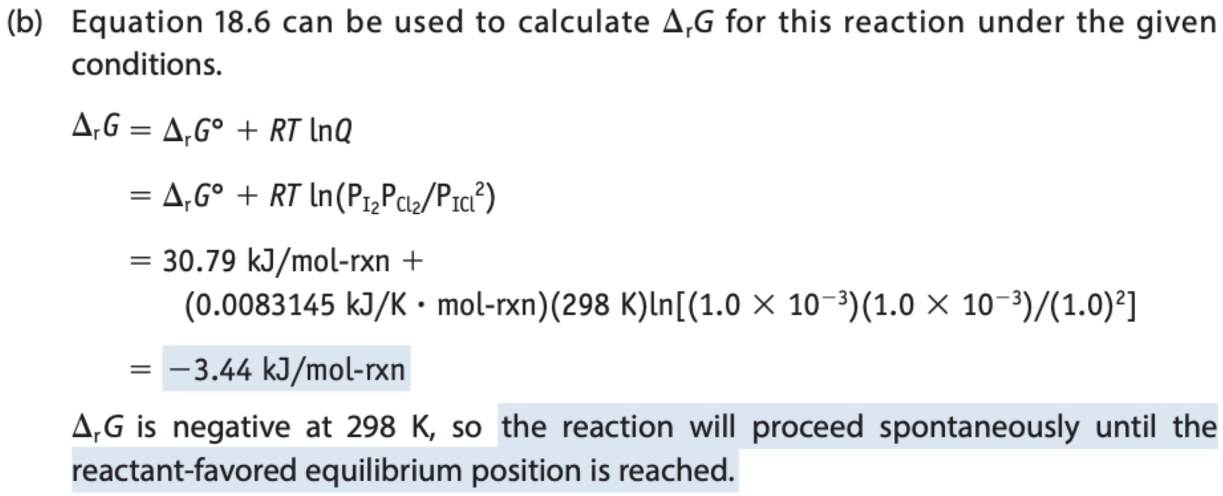
$$= \{(1 \text{ mol } I_2(g)/\text{mol-rxn})\ \Delta_f G°[I_2(g)] + (1 \text{ mol } Cl_2(g)/\text{mol-rxn})\ \Delta_f G°[Cl_2(g)]\} - (2 \text{ mol ICl}(g)/\text{mol-rxn})\ \Delta_f G°[\text{ICl}(g)]$$

$$= [(1 \text{ mol } I_2(g)/\text{mol-rxn})(19.33 \text{ kJ/mol}) + (1 \text{ mol } Cl_2(g)/\text{mol-rxn})(0 \text{ kJ/mol})] - (2 \text{ mol ICl}(g)/\text{mol-rxn})(-5.73 \text{ kJ/mol})$$

$$= 30.79 \text{ kJ/mol-rxn}$$

$\Delta_r G°$ is positive at 298 K, so the reaction is predicted to be reactant-favored at equilibrium.

b) Calculate the value of $\Delta_r G$ at 298 K for this reaction if the reactant and products are mixed with the following partial pressures: 1.0 atm ICl, 1.0×10^{-3} atm I_2, and 1.0×10^{-3} atm Cl_2. Is the reaction spontaneous under these conditions?



(b) Equation 18.6 can be used to calculate $\Delta_r G$ for this reaction under the given conditions.

$$\Delta_r G = \Delta_r G° + RT \ln Q$$

$$= \Delta_r G° + RT \ln(P_{I_2} P_{Cl_2} / P_{ICl}{}^2)$$

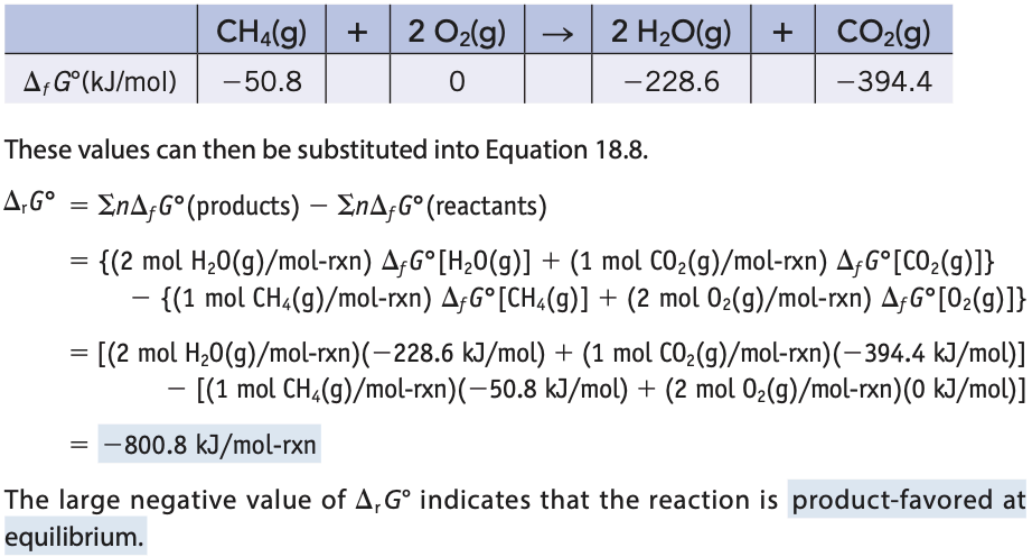
$$= 30.79 \text{ kJ/mol-rxn} + (0.0083145 \text{ kJ/K} \cdot \text{mol-rxn})(298 \text{ K}) \ln[(1.0 \times 10^{-3})(1.0 \times 10^{-3})/(1.0)^2]$$

$$= -3.44 \text{ kJ/mol-rxn}$$

$\Delta_r G$ is negative at 298 K, so the reaction will proceed spontaneously until the reactant-favored equilibrium position is reached.

6) Calculate the standard free energy change for burning one mole of methane using values for standard free energies of formation of the products and reactants and assuming the products are all gases. Is the reaction product-favored at equilibrium?

$$CH_4(g) + 2\ O_2(g) \rightarrow 2\ H_2O(g) + CO_2(g)$$



	$CH_4(g)$	+	$2\ O_2(g)$	→	$2\ H_2O(g)$	+	$CO_2(g)$
$\Delta_f G°$(kJ/mol)	−50.8		0		−228.6		−394.4

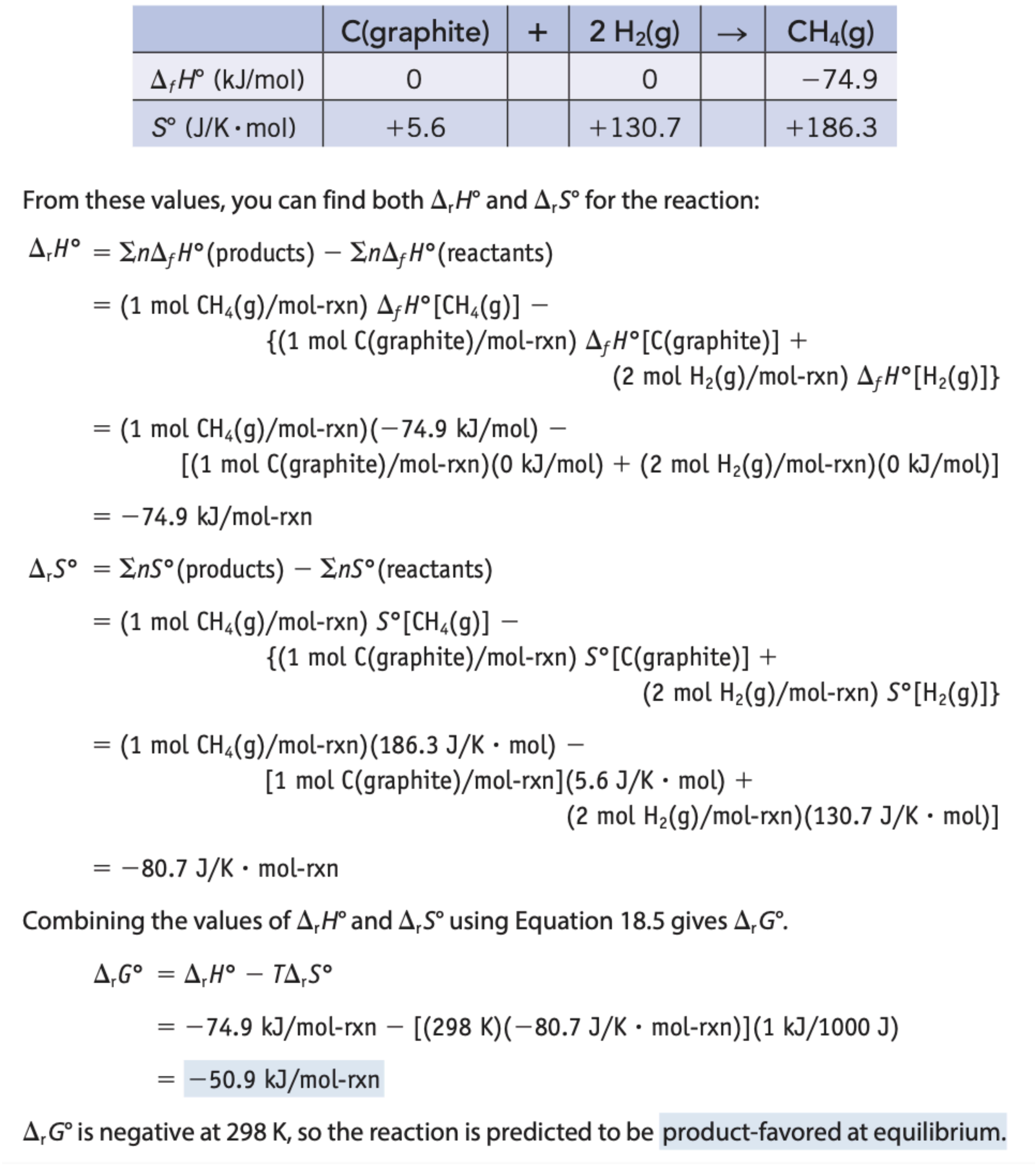
These values can then be substituted into Equation 18.8.

$$\begin{aligned}\Delta_r G° &= \Sigma n \Delta_f G°(\text{products}) - \Sigma n \Delta_f G°(\text{reactants}) \\ &= \{(2\text{ mol }H_2O(g)/\text{mol-rxn})\ \Delta_f G°[H_2O(g)] + (1\text{ mol }CO_2(g)/\text{mol-rxn})\ \Delta_f G°[CO_2(g)]\} \\ &\quad - \{(1\text{ mol }CH_4(g)/\text{mol-rxn})\ \Delta_f G°[CH_4(g)] + (2\text{ mol }O_2(g)/\text{mol-rxn})\ \Delta_f G°[O_2(g)]\} \\ &= [(2\text{ mol }H_2O(g)/\text{mol-rxn})(-228.6\text{ kJ/mol}) + (1\text{ mol }CO_2(g)/\text{mol-rxn})(-394.4\text{ kJ/mol})] \\ &\quad - [(1\text{ mol }CH_4(g)/\text{mol-rxn})(-50.8\text{ kJ/mol}) + (2\text{ mol }O_2(g)/\text{mol-rxn})(0\text{ kJ/mol})] \\ &= -800.8\text{ kJ/mol-rxn}\end{aligned}$$

The large negative value of $\Delta_r G°$ indicates that the reaction is product-favored at equilibrium.

7) Calculate the standard free energy change, $\Delta_r G°$, for the formation of methane from carbon and hydrogen at 298 K, using tabulated values of $\Delta_f H°$ and S°. Is the reaction product-favored or reactant-favored at equilibrium?

$$C(\text{graphite}) + 2\ H_2(g) \rightarrow CH_4(g)$$



	C(graphite)	+	$2\ H_2(g)$	→	$CH_4(g)$
$\Delta_f H°$ (kJ/mol)	0		0		−74.9
$S°$ (J/K·mol)	+5.6		+130.7		+186.3

From these values, you can find both $\Delta_r H°$ and $\Delta_r S°$ for the reaction:

$$\begin{aligned}\Delta_r H° &= \Sigma n\Delta_f H°(\text{products}) - \Sigma n\Delta_f H°(\text{reactants})\\ &= (1\ \text{mol}\ CH_4(g)/\text{mol-rxn})\ \Delta_f H°[CH_4(g)] - \\ &\qquad \{(1\ \text{mol C(graphite)/mol-rxn})\ \Delta_f H°[\text{C(graphite)}] + \\ &\qquad\qquad (2\ \text{mol}\ H_2(g)/\text{mol-rxn})\ \Delta_f H°[H_2(g)]\}\\ &= (1\ \text{mol}\ CH_4(g)/\text{mol-rxn})(-74.9\ \text{kJ/mol}) - \\ &\qquad [(1\ \text{mol C(graphite)/mol-rxn})(0\ \text{kJ/mol}) + (2\ \text{mol}\ H_2(g)/\text{mol-rxn})(0\ \text{kJ/mol})]\\ &= -74.9\ \text{kJ/mol-rxn}\end{aligned}$$

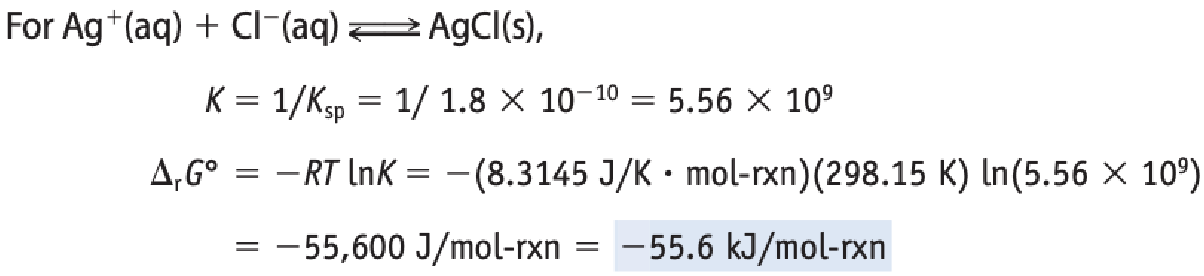
$$\begin{aligned}\Delta_r S° &= \Sigma nS°(\text{products}) - \Sigma nS°(\text{reactants})\\ &= (1\ \text{mol}\ CH_4(g)/\text{mol-rxn})\ S°[CH_4(g)] - \\ &\qquad \{(1\ \text{mol C(graphite)/mol-rxn})\ S°[\text{C(graphite)}] + \\ &\qquad\qquad (2\ \text{mol}\ H_2(g)/\text{mol-rxn})\ S°[H_2(g)]\}\\ &= (1\ \text{mol}\ CH_4(g)/\text{mol-rxn})(186.3\ \text{J/K}\cdot\text{mol}) - \\ &\qquad [1\ \text{mol C(graphite)/mol-rxn}](5.6\ \text{J/K}\cdot\text{mol}) + \\ &\qquad\qquad (2\ \text{mol}\ H_2(g)/\text{mol-rxn})(130.7\ \text{J/K}\cdot\text{mol})]\\ &= -80.7\ \text{J/K}\cdot\text{mol-rxn}\end{aligned}$$

Combining the values of $\Delta_r H°$ and $\Delta_r S°$ using Equation 18.5 gives $\Delta_r G°$.

$$\begin{aligned}\Delta_r G° &= \Delta_r H° - T\Delta_r S°\\ &= -74.9\ \text{kJ/mol-rxn} - [(298\ \text{K})(-80.7\ \text{J/K}\cdot\text{mol-rxn})](1\ \text{kJ}/1000\ \text{J})\\ &= -50.9\ \text{kJ/mol-rxn}\end{aligned}$$

$\Delta_r G°$ is negative at 298 K, so the reaction is predicted to be product-favored at equilibrium.

8) The value of K_{sp} for AgCl(s) at 25 °C is 1.8×10^{-10}. Determine $\Delta_r G°$ for the process $Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$ at 298.15 K.



For $Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$,

$$K = 1/K_{sp} = 1/\ 1.8 \times 10^{-10} = 5.56 \times 10^{9}$$

$$\Delta_r G° = -RT \ln K = -(8.3145\ \text{J/K} \cdot \text{mol-rxn})(298.15\ \text{K}) \ln(5.56 \times 10^{9})$$

$$= -55{,}600\ \text{J/mol-rxn} = -55.6\ \text{kJ/mol-rxn}$$