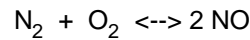


Solutions to: Thermodynamics Homework Problem Set

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1. Nitrogen Oxides are very important species in atmospheric chemistry. They are critical for a number of reactions that contribute to photochemical smog. The major anthropogenic (man made) source of NO is from the following reaction:



In this problem you will study the temperature dependence of this reaction to learn how the emission of NO may be reduced. Answer the following questions (assume that H is constant at each temperature):

a. What is ΔH_{rxn} , ΔS_{rxn} , ΔG_{rxn} , and K (We will assume that ΔH_{rxn} and ΔS_{rxn} do not change with temperature. This is not strictly true and in more advanced courses you will learn how to account for these changes.) at 25, 1000, 2000, and 3000 °C

Constants:

$$\text{kJ} := 10^3 \cdot \text{joule}$$

$$\underline{\underline{R}} := 8.31441 \cdot \frac{\text{joule}}{\text{K}}$$

$$\Delta H_{\text{rxn}} := \left[(2 \cdot \text{mole}) \cdot \left(90.4 \cdot \frac{\text{kJ}}{\text{mole}} \right) \right] - \left[(1 \cdot \text{mole}) \cdot \left(0 \cdot \frac{\text{kJ}}{\text{mole}} \right) + (1 \cdot \text{mole}) \cdot \left(0 \cdot \frac{\text{kJ}}{\text{mole}} \right) \right]$$

$$\Delta S_{\text{rxn}} := \left[(2 \cdot \text{mole}) \cdot \left(210.62 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}} \right) \right] - \left[(1 \cdot \text{mole}) \cdot \left(191.5 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}} \right) + (1 \cdot \text{mole}) \cdot \left(205.15 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}} \right) \right]$$

i. 25 °C $\underline{\underline{T}} := (25 + 273.15) \cdot \text{K}$

$$\Delta H_{\text{rxn}} = 180.8 \text{ kJ}$$

$$\Delta S_{\text{rxn}} = 24.59 \text{ joule} \cdot \text{K}^{-1}$$

$$\Delta G_{\text{rxn}} := \Delta H_{\text{rxn}} - T \cdot \Delta S_{\text{rxn}}$$

$$\Delta G_{\text{rxn}} = 173.468 \text{ kJ}$$

$$\Delta G_{\text{rxn}} = -R \cdot T \cdot \ln(K_{\text{eq}})$$

$$K_{25} := \exp\left(\frac{-\Delta G_{\text{rxn}}}{R \cdot T}\right)$$

$$K_{25} = 4.069 \times 10^{-31}$$

ii. $1000\text{ }^{\circ}\text{C}$ $T := (1000 + 273.15) \cdot \text{K}$

$$\Delta H_{\text{rxn}} = 180.8 \text{ kJ}$$

$$\Delta S_{\text{rxn}} = 24.59 \text{ joule} \cdot \text{K}^{-1}$$

$$\Delta G_{\text{rxn}} := \Delta H_{\text{rxn}} - T \cdot \Delta S_{\text{rxn}}$$

$$\Delta G_{\text{rxn}} = 149.493 \text{ kJ}$$

$$K_{1000} := \exp\left(\frac{-\Delta G_{\text{rxn}}}{R \cdot T}\right)$$

$$K_{1000} = 7.357 \times 10^{-7}$$

iii. $2000\text{ }^{\circ}\text{C}$ $T := (2000 + 273.15) \cdot \text{K}$

$$\Delta H_{\text{rxn}} = 180.8 \text{ kJ}$$

$$\Delta S_{\text{rxn}} = 24.59 \text{ joule} \cdot \text{K}^{-1}$$

$$\Delta G_{\text{rxn}} := \Delta H_{\text{rxn}} - T \cdot \Delta S_{\text{rxn}}$$

$$\Delta G_{\text{rxn}} = 124.903 \text{ kJ}$$

$$K_{2000} := \exp\left(\frac{-\Delta G_{\text{rxn}}}{R \cdot T}\right)$$

$$K_{2000} = 1.349 \times 10^{-3}$$

iv. $3000\text{ }^{\circ}\text{C}$ $T := (3000 + 273.15) \cdot \text{K}$

$$\Delta H_{\text{rxn}} = 180.8 \text{ kJ}$$

$$\Delta S_{\text{rxn}} = 24.59 \text{ joule} \cdot \text{K}^{-1}$$

$$\Delta G_{\text{rxn}} := \Delta H_{\text{rxn}} - T \cdot \Delta S_{\text{rxn}}$$

$$\Delta G_{\text{rxn}} = 100.313 \text{ kJ}$$

$$K_{3000} := \exp\left(\frac{-\Delta G_{\text{rxn}}}{R \cdot T}\right)$$

$$K_{3000} = 0.025$$

b. The atmospheric pressure of N₂ is 0.80 atm and O₂ is 0.20 atm. Determine the equilibrium pressure of NO at each temperature.

$$K = \frac{P_{\text{NO}}^2}{P_{\text{N}_2} \cdot P_{\text{O}_2}}$$

$$P_{\text{NO}} = \sqrt{K \cdot P_{\text{N}_2} \cdot P_{\text{O}_2}}$$

$$P_{\text{N}_2} := 0.80 \cdot \text{atm}$$

$$P_{\text{O}_2} := 0.20 \cdot \text{atm}$$

i. 25 °C $T := (25 + 273.15) \cdot \text{K}$

$$P_{\text{NO}} := \sqrt{K_{25} \cdot P_{\text{N}_2} \cdot P_{\text{O}_2}}$$

$$P_{\text{NO}} = 2.551 \times 10^{-16} \text{ atm}$$

ii. 1000 °C $T := (1000 + 273.15) \cdot \text{K}$

$$P_{\text{NO}} := \sqrt{K_{1000} \cdot P_{\text{N}_2} \cdot P_{\text{O}_2}}$$

$$P_{\text{NO}} = 3.431 \times 10^{-4} \text{ atm}$$

iii. 2000 °C $T := (2000 + 273.15) \cdot \text{K}$

$$P_{\text{NO}} := \sqrt{K_{2000} \cdot P_{\text{N}_2} \cdot P_{\text{O}_2}}$$

$$P_{\text{NO}} = 0.015 \text{ atm}$$

iv. 3000 °C $T := (3000 + 273.15) \cdot \text{K}$

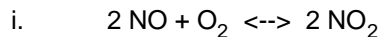
$$P_{\text{NO}} := \sqrt{K_{3000} \cdot P_{\text{N}_2} \cdot P_{\text{O}_2}}$$

$$P_{\text{NO}} = 0.063 \text{ atm}$$

c. At high temperatures the above reaction is fast enough that the system can reach equilibrium. When exhaust gases leave a combustion chamber (an automobile, truck, boiler, or power plant) the air quickly cools. At the lower temperature the reaction is much slower so the reaction does not return to equilibrium. Would lowering the combustion temperature from 3000 °C to 2000 °C or even to 1000 °C have any effect on the NO emission?

Yes at lower temperatures, the equilibrium is much less favorable. At higher temperatures more NO is produced. Since the system does not equilibrate quickly at ambient temperatures, this high NO concentration remains for an extended time period after the exhaust leaves the combustion chamber. Although the equilibrium favors lower NO concentrations at ambient temperatures, the return to equilibrium is slow. As we will discuss in the next chapter, the Kinetics (or rate) of the NO returning to equilibrium may be increased by using a catalyst. This is one of the functions of the catalytic converter in automobiles.

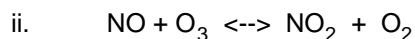
d. Dr. Madigoski and I recently purchased an instrument to determine the concentration of NO and NO₂ with funds provided by a grant from the National Science Foundation. Based upon the Gibbs free energy, which of the following reactions is a feasible mechanism for converting NO into NO₂?



$$\Delta G_{\text{rxn}} := \left[(2 \cdot \text{mole}) \cdot \left(51.84 \cdot \frac{\text{kJ}}{\text{mole}} \right) \right] - \left[(2 \cdot \text{mole}) \cdot \left(86.7 \cdot \frac{\text{kJ}}{\text{mole}} \right) + (1 \cdot \text{mole}) \cdot \left(0 \cdot \frac{\text{kJ}}{\text{mole}} \right) \right]$$

$$\Delta G_{\text{rxn}} = -69.72 \text{ kJ}$$

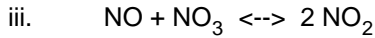
ΔG values are from Kask and Rawn. Since ΔG_{rxn} is negative, the reaction is spontaneous as written so this mechanism is one possible mechanism.



$$\Delta G_{\text{rxn}} := \left[(1 \cdot \text{mole}) \cdot \left(51.84 \cdot \frac{\text{kJ}}{\text{mole}} \right) + (1 \cdot \text{mole}) \cdot \left(0 \cdot \frac{\text{kJ}}{\text{mole}} \right) \right] - \left[(1 \cdot \text{mole}) \cdot \left(86.7 \cdot \frac{\text{kJ}}{\text{mole}} \right) + (1 \cdot \text{mole}) \cdot \left(163.4 \cdot \frac{\text{kJ}}{\text{mole}} \right) \right]$$

$$\Delta G_{\text{rxn}} = -198.26 \text{ kJ}$$

ΔG values are from Kask and Rawn. Since ΔG_{rxn} is negative, the reaction is spontaneous as written so this mechanism is one possible mechanism.

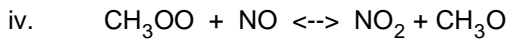


No thermodynamic data is available in your textbook for NO_3 . The following values are from the NIST S&P database.

$$\Delta H_{\text{rxn}} := \left[(2 \cdot \text{mole}) \cdot \left(33.1 \cdot \frac{\text{kJ}}{\text{mole}} \right) \right] - \left[(1 \cdot \text{mole}) \cdot \left(91.3 \cdot \frac{\text{kJ}}{\text{mole}} \right) + (1 \cdot \text{mole}) \cdot \left(70.7 \cdot \frac{\text{kJ}}{\text{mole}} \right) \right]$$

$$\Delta H_{\text{rxn}} = -95.8 \text{ kJ}$$

I was unable to determine the value of S° for NO_3 , so it is not possible to calculate ΔG_{rxn} with the information that I have available. More extensive tables of thermodynamic data are available. However, since ΔH_{rxn} is negative and in a gas phase reaction like this the number of moles of gas is unchanged so ΔS is probably very close to 0. From this it is very likely that this reaction is thermodynamically possible.



I was unable to find any thermochemical data for CH_3COO so it is not possible to make any judgment about this mechanism (for now).

2. Calculate ΔG at 20 °C for the reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2 \text{HI}$. Starting with 1.0 atm H_2 and 1.0 atm I_2 . What is ΔG when 0.1%, 1%, 10%, 50%, 90%, 99% and 99.9% has reacted:

$$\Delta G_0 := \left[(2 \cdot \text{mole}) \cdot \left(1.30 \cdot \frac{\text{kJ}}{\text{mole}} \right) \right] - \left[(1 \cdot \text{mole}) \cdot \left(19.4 \cdot \frac{\text{kJ}}{\text{mole}} \right) + (1 \cdot \text{mole}) \cdot \left(0 \cdot \frac{\text{kJ}}{\text{mole}} \right) \right]$$

$$\Delta G_0 = -16.8 \text{ kJ}$$

$$T := (20 + 273.15) \cdot \text{K}$$

a. 0.1% has reacted

$$P_{\text{H}_2_initial} := 1 \cdot \text{atm}$$

$$P_{\text{I}_2_initial} := 1 \cdot \text{atm}$$

$$\text{reacted} := (0.1\%) \cdot P_{\text{I}_2_initial}$$

$$Q(a) := \frac{(2 \cdot a)^2}{(P_{\text{H}_2_initial} - a) \cdot (P_{\text{I}_2_initial} - a)}$$

$$\Delta G_{\text{rxn}} := \Delta G_{\text{O}} + R \cdot T \cdot \ln(Q(\text{reacted}))$$

$$\Delta G_{\text{rxn}} = -47.09 \text{ kJ}$$

b. 1% has reacted

$$\text{reacted} := (1\%) \cdot P_{I2_initial}$$

$$\Delta G_{rxn} := \Delta G_0 + R \cdot T \cdot \ln(Q(\text{reacted})) \quad \Delta G_{rxn} = -35.821 \text{ kJ}$$

c. 10% has reacted

$$\text{reacted} := (10\%) \cdot P_{I2_initial}$$

$$\Delta G_{rxn} := \Delta G_0 + R \cdot T \cdot \ln(Q(\text{reacted})) \quad \Delta G_{rxn} = -24.132 \text{ kJ}$$

d. 50% has reacted

$$\text{reacted} := (50\%) \cdot P_{I2_initial}$$

$$\Delta G_{rxn} := \Delta G_0 + R \cdot T \cdot \ln(Q(\text{reacted})) \quad \Delta G_{rxn} = -13.421 \text{ kJ}$$

e. 90% has reacted

$$\text{reacted} := (90\%) \cdot P_{I2_initial}$$

$$\Delta G_{rxn} := \Delta G_0 + R \cdot T \cdot \ln(Q(\text{reacted})) \quad \Delta G_{rxn} = -2.71 \text{ kJ}$$

f. 99% has reacted

$$\text{reacted} := (99\%) \cdot P_{I2_initial}$$

$$\Delta G_{rxn} := \Delta G_0 + R \cdot T \cdot \ln(Q(\text{reacted})) \quad \Delta G_{rxn} = 8.979 \text{ kJ}$$

g. 99.9% has reacted

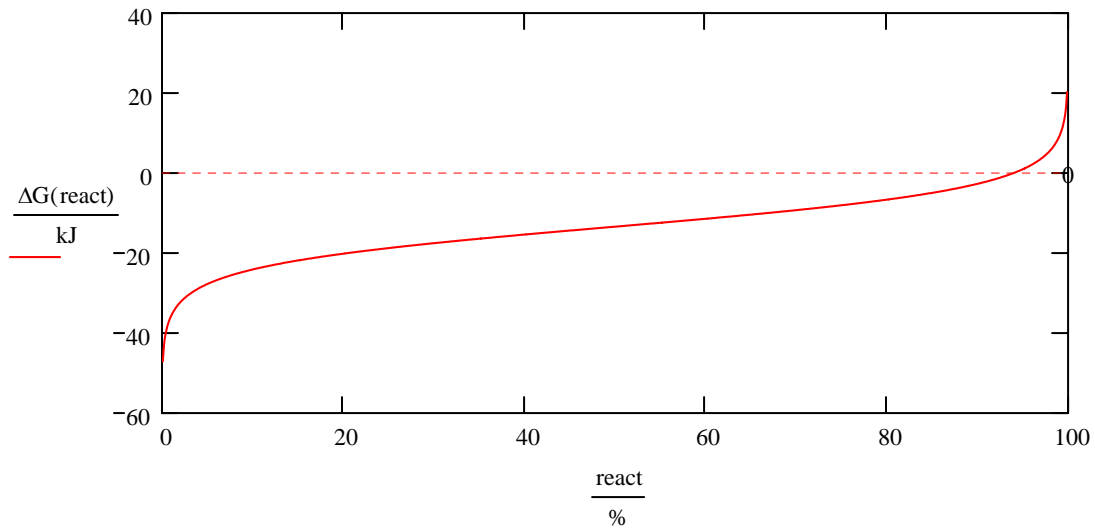
$$\text{reacted} := (99.9\%) \cdot P_{I2_initial}$$

$$\Delta G_{rxn} := \Delta G_0 + R \cdot T \cdot \ln(Q(\text{reacted})) \quad \Delta G_{rxn} = 20.248 \text{ kJ}$$

This exercise was to show how the Gibbs free energy changes with the concentrations of reactants and products. From this you should see that there is a point when this reaction is between 90% and 99% complete that the free energy is 0. At this point the reaction is at equilibrium. Below is a graph that shows this relationship.

react := 0.1%, 0.2% .. 99.9%

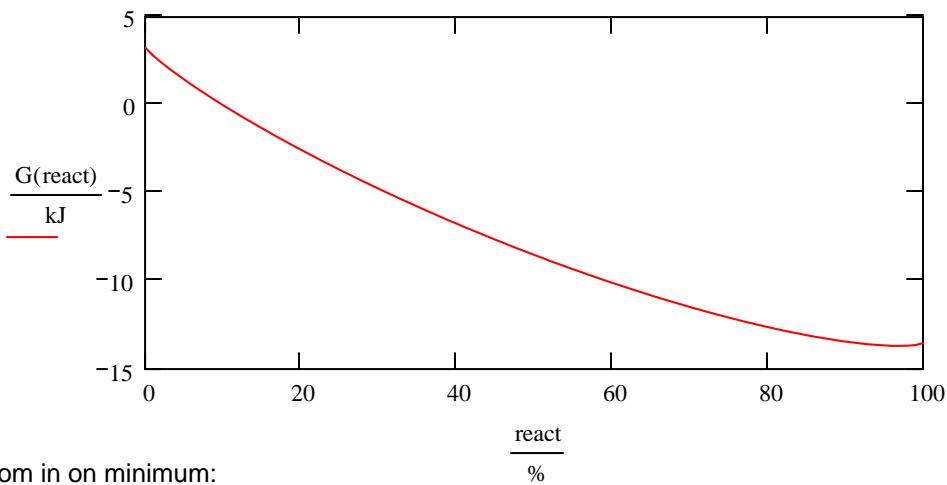
$$\Delta G(a) := \Delta G_0 + R \cdot T \cdot \ln \left[\frac{(2 \cdot a \cdot P_{I2_initial})^2}{(P_{H2_initial} - a \cdot P_{I2_initial}) \cdot (P_{I2_initial} - a \cdot P_{I2_initial})} \right]$$



For those of you who have taken calculus, the curve above is actually the derivative of the free energy as a function of the "reaction coordinate" Or how much has reacted. It is possible to derive the free energy (not ΔG) vs. reaction coordinate by integrating the above expression. Since ΔG is the change in G , it is the equivalent to the slope of a graph of the free energy curve. If you have taken enough calculus you will recognize that if I integrate the above curve it will give me the free energy curve. This will give:

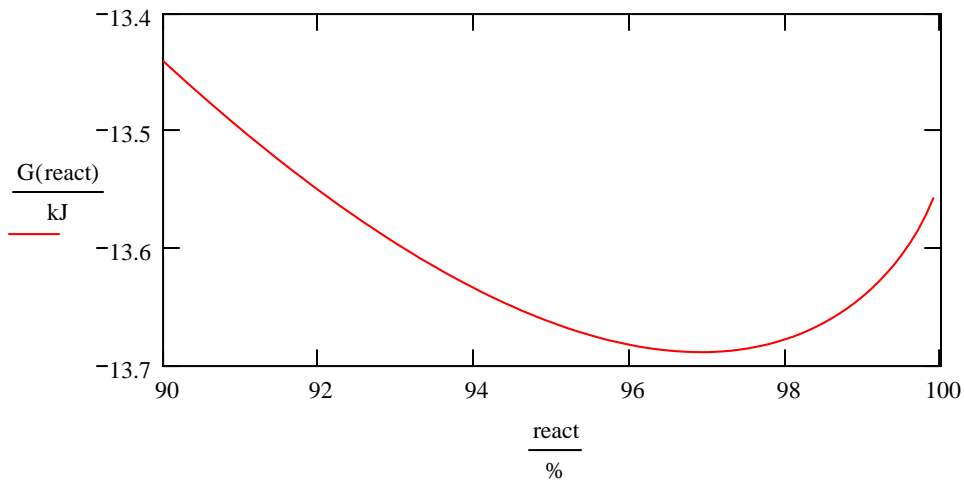
$$G(a) := \int_{0.1}^a \Delta G_0 + R \cdot T \cdot \ln \left[\frac{(a \cdot P_{I2_initial})^2}{(P_{H2_initial} - a \cdot P_{I2_initial}) \cdot (P_{I2_initial} - a \cdot P_{I2_initial})} \right] da$$

react := 0%, 1% .. 100%



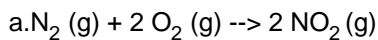
Zoom in on minimum:

react := 90%, 90.1% .. 99.9%



The minimum of the free energy curve is the equilibrium condition. Recall that since this is a minimum, its slope is zero. Which is why this corresponds to the zero crossing of the earlier graph.

3. Using values from your textbook calculate ΔS° and ΔG° for the following reactions:

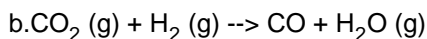


$$\Delta S_{\text{rxn}} := \left[(2 \cdot \text{mole}) \cdot \left(240.06 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}} \right) \right] - \left[(1 \cdot \text{mole}) \cdot \left(191.61 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}} \right) + (1 \cdot \text{mole}) \cdot \left(205.138 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}} \right) \right]$$

$$\Delta G_{\text{rxn}} := \left[(2 \cdot \text{mole}) \cdot \left(51.31 \cdot \frac{\text{kJ}}{\text{mole}} \right) \right] - \left[(1 \cdot \text{mole}) \cdot \left(0 \cdot \frac{\text{kJ}}{\text{mole}} \right) + (1 \cdot \text{mole}) \cdot \left(0 \cdot \frac{\text{kJ}}{\text{mole}} \right) \right]$$

$$\Delta S_{\text{rxn}} = 83.372 \text{ joule} \cdot \text{K}^{-1}$$

$$\Delta G_{\text{rxn}} = 1.026 \times 10^5 \text{ K joule} \cdot \text{K}^{-1}$$



$$\Delta S_{\text{rxn}} := \left[(1 \cdot \text{mole}) \cdot \left(197.674 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}} \right) + (1 \cdot \text{mole}) \cdot \left(188.825 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}} \right) \right] \dots$$

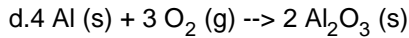
$$+ - \left[(1 \cdot \text{mole}) \cdot \left(213.74 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}} \right) + (1 \cdot \text{mole}) \cdot \left(130.684 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}} \right) \right]$$

$$\Delta G_{\text{rxn}} := \left[(1 \cdot \text{mole}) \cdot \left(-137.168 \cdot \frac{\text{kJ}}{\text{mole}} \right) + (1 \cdot \text{mole}) \cdot \left(-228.572 \cdot \frac{\text{kJ}}{\text{mole}} \right) \right] \dots$$

$$+ - \left[(1 \cdot \text{mole}) \cdot \left(-394.359 \cdot \frac{\text{kJ}}{\text{mole}} \right) + (1 \cdot \text{mole}) \cdot \left(0 \cdot \frac{\text{kJ}}{\text{mole}} \right) \right]$$

$$\Delta S_{\text{rxn}} = 42.075 \text{ joule} \cdot \text{K}^{-1}$$

$$\Delta G_{\text{rxn}} = 2.862 \times 10^4 \text{ K joule} \cdot \text{K}^{-1}$$

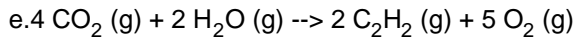


$$\Delta S_{\text{rxn}} := \left[(2 \cdot \text{mole}) \cdot \left(50.92 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}} \right) \right] - \left[(4 \cdot \text{mole}) \cdot \left(28.3 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}} \right) + (3 \cdot \text{mole}) \cdot \left(205.138 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}} \right) \right]$$

$$\Delta G_{\text{rxn}} := \left[(2 \cdot \text{mole}) \cdot \left(-1582.3 \cdot \frac{\text{kJ}}{\text{mole}} \right) \right] - \left[(4 \cdot \text{mole}) \cdot \left(0 \cdot \frac{\text{kJ}}{\text{mole}} \right) + (3 \cdot \text{mole}) \cdot \left(0 \cdot \frac{\text{kJ}}{\text{mole}} \right) \right]$$

$$\Delta S_{\text{rxn}} = -626.774 \text{ joule} \cdot \text{K}^{-1}$$

$$\Delta G_{\text{rxn}} = -3.165 \times 10^6 \text{ K joule} \cdot \text{K}^{-1}$$



$$\Delta S_{\text{rxn}} := \left[(2 \cdot \text{mole}) \cdot \left(200.94 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}} \right) + (5 \cdot \text{mole}) \cdot \left(205.138 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}} \right) \right] \dots$$

$$+ \left[(4 \cdot \text{mole}) \cdot \left(213.74 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}} \right) + (2 \cdot \text{mole}) \cdot \left(188.825 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}} \right) \right]$$

$$\Delta G_{\text{rxn}} := \left[(2 \cdot \text{mole}) \cdot \left(209.20 \cdot \frac{\text{kJ}}{\text{mole}} \right) + (5 \cdot \text{mole}) \cdot \left(0 \cdot \frac{\text{kJ}}{\text{mole}} \right) \right] \dots$$

$$+ \left[(4 \cdot \text{mole}) \cdot \left(-394.359 \cdot \frac{\text{kJ}}{\text{mole}} \right) + (2 \cdot \text{mole}) \cdot \left(-228.572 \cdot \frac{\text{kJ}}{\text{mole}} \right) \right]$$

$$\Delta S_{\text{rxn}} = 194.96 \text{ joule} \cdot \text{K}^{-1}$$

$$\Delta G_{\text{rxn}} = 2.453 \times 10^6 \text{ K joule} \cdot \text{K}^{-1}$$

