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:

\[ \text{N}_2 + \text{O}_2 \rightleftharpoons 2 \text{NO} \]

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 \( \Delta H_{\text{rxn}} \), \( \Delta S_{\text{rxn}} \), \( \Delta G_{\text{rxn}} \), and \( K \) (We will assume that \( \Delta H_{\text{rxn}} \) and \( \Delta S_{\text{rxn}} \) 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:

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

\[ R := 8.31441 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}} \]

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

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

i. \( 25 \degree C \quad T := (25 + 273.15) \cdot K \)

\[ \Delta H_{\text{rxn}} = 180.8 \cdot \text{kJ} \]

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

\[ \Delta G_{\text{rxn}} := \Delta H_{\text{rxn}} - T \cdot \Delta S_{\text{rxn}} \quad \Delta G_{\text{rxn}} = 173.468 \cdot \text{kJ} \]

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

\[ K_{25} := \exp \left( \frac{-\Delta G_{\text{rxn}}}{R \cdot T} \right) \quad K_{25} = 4.069 \times 10^{-31} \]
ii. 1000 °C $T := (1000 + 273.15) \cdot \text{K}$

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

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

$\Delta G_{\text{rxn}} := \Delta H_{\text{rxn}} - T \cdot \Delta S_{\text{rxn}}$  \hspace{1cm} $\Delta G_{\text{rxn}} = 149.493 \text{kJ}$

$K_{1000} := \exp\left(\frac{-\Delta G_{\text{rxn}}}{R \cdot T}\right)$  \hspace{1cm} $K_{1000} = 7.357 \times 10^{-7}$

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

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

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

$\Delta G_{\text{rxn}} := \Delta H_{\text{rxn}} - T \cdot \Delta S_{\text{rxn}}$  \hspace{1cm} $\Delta G_{\text{rxn}} = 124.903 \text{kJ}$

$K_{2000} := \exp\left(\frac{-\Delta G_{\text{rxn}}}{R \cdot T}\right)$  \hspace{1cm} $K_{2000} = 1.349 \times 10^{-3}$

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

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

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

$\Delta G_{\text{rxn}} := \Delta H_{\text{rxn}} - T \cdot \Delta S_{\text{rxn}}$  \hspace{1cm} $\Delta G_{\text{rxn}} = 100.313 \text{kJ}$

$K_{3000} := \exp\left(\frac{-\Delta G_{\text{rxn}}}{R \cdot T}\right)$  \hspace{1cm} $K_{3000} = 0.025$
b. The atmospheric pressure of N\(_2\) is 0.80 atm and O\(_2\) is 0.20 atm. Determine the equilibrium pressure of NO at each temperature.

\[ K = \frac{P_{NO}^2}{P_{N2} \cdot P_{O2}} \]

\[ P_{NO} = \sqrt{K \cdot P_{N2} \cdot P_{O2}} \]

\( P_{N2} := 0.80 \text{ atm} \)
\( P_{O2} := 0.20 \text{ atm} \)

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

\[ P_{NO} := \sqrt{K_{25} \cdot P_{N2} \cdot P_{O2}} \]
\[ P_{NO} = 2.551 \times 10^{-16} \text{ atm} \]

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

\[ P_{NO} := \sqrt{K_{1000} \cdot P_{N2} \cdot P_{O2}} \]
\[ P_{NO} = 3.431 \times 10^{-4} \text{ atm} \]

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

\[ P_{NO} := \sqrt{K_{2000} \cdot P_{N2} \cdot P_{O2}} \]
\[ P_{NO} = 0.015 \text{ atm} \]

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

\[ P_{NO} := \sqrt{K_{3000} \cdot P_{N2} \cdot P_{O2}} \]
\[ P_{NO} = 0.063 \text{ atm} \]
c. At high temperatures this reaction fast and reaches equilibrium quickly, but when exhaust
gases cool the reaction is very slow and the system stays at the high temperature equilibrium. Would
lowering the combustion temperature from 3000 °C to 2000 °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. The concentration of NO is normally determined with an instrument that first converts it to
NO2. Based upon the Gibbs free energy, could the following reaction be used to convert NO into NO2 at
ambient temperatures?

\[ NO + O_3 \rightarrow 2 NO_2 + O_2 \]

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

\[
\Delta G_{\text{rxn}} = -198.26 \ \text{kJ}
\]

\( \Delta G \) values are from Kask and Rawn. Since \( \Delta G_{\text{rxn}} \) is negative, the reaction is spontaneous as
written so this mechanism is one possible mechanism.
2. Calculate $\Delta G$ at 20 °C for the reaction $\text{H}_2 + \text{I}_2 \leftrightarrow 2 \text{HI}$. Starting with 1.0 atm $\text{H}_2$ and 1.0 atm $\text{I}_2$.

What is $\Delta G$ when 0.1%, 1%, 10%, 50%, 90%, 99% and 99.9% has reacted:

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

\[
\Delta G_0 = -16.8 \cdot \text{kJ}
\]

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

a. 1.0 % has reacted

\[
P_{\text{H}_2_{\text{initial}}} := 1 \cdot \text{atm}
\]

\[
P_{\text{I}_2_{\text{initial}}} := 1 \cdot \text{atm}
\]

\[
\text{reacted} := (1 \cdot \%) \cdot P_{\text{I}_2_{\text{initial}}}
\]

\[
Q(a) := \frac{(2 \cdot a)^2}{(P_{\text{H}_2_{\text{initial}}} - a) \cdot (P_{\text{I}_2_{\text{initial}}} - a)}
\]

\[
\Delta G_{\text{rxn}} := \Delta G_0 + R \cdot T \cdot \ln(Q(\text{reacted}))
\]

\[
\Delta G_{\text{rxn}} = -35.821 \cdot \text{kJ}
\]

c. 10% has reacted

\[
\text{reacted} := (10 \cdot \%) \cdot P_{\text{I}_2_{\text{initial}}}
\]

\[
\Delta G_{\text{rxn}} := \Delta G_0 + R \cdot T \cdot \ln(Q(\text{reacted}))
\]

\[
\Delta G_{\text{rxn}} = -24.132 \cdot \text{kJ}
\]

e. 90% has reacted

\[
\text{reacted} := (90 \cdot \%) \cdot P_{\text{I}_2_{\text{initial}}}
\]

\[
\Delta G_{\text{rxn}} := \Delta G_0 + R \cdot T \cdot \ln(Q(\text{reacted}))
\]

\[
\Delta G_{\text{rxn}} = -2.71 \cdot \text{kJ}
\]

f. 99% has reacted

\[
\text{reacted} := (99 \cdot \%) \cdot P_{\text{I}_2_{\text{initial}}}
\]

\[
\Delta G_{\text{rxn}} := \Delta G_0 + R \cdot T \cdot \ln(Q(\text{reacted}))
\]

\[
\Delta G_{\text{rxn}} = 8.979 \cdot \text{kJ}
\]
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.

\[
\Delta G(a) := \Delta G_0 + R \cdot T \cdot \ln \left( \frac{(2 \cdot a \cdot P_{I2_{\text{initial}}})^2}{(P_{H2_{\text{initial}}} - a \cdot P_{I2_{\text{initial}}}) \cdot (P_{I2_{\text{initial}}} - a \cdot P_{I2_{\text{initial}}})} \right)
\]

\[
\text{react} := 0.1\% , 0.2\% , ..., 99.9\%
\]
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 $\Delta G$) vs. reaction coordinate by integrating the above expression. Since $\Delta G$ 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:

$$G(a) := \int_{0.1}^{a} \left[ \Delta G_0 + R \cdot T \cdot \ln \left( \frac{\left( a \cdot P_{I2\_initial}\right)^2}{(P_{I2\_initial} - a \cdot P_{I2\_initial})^2} \right) \right] da$$

$react := 0\,-\,\%$,$1\,-\,\%$,$\ldots$,$100\,-\,\%$

Zoom in on minimum:

$react := 90\,-\,\%$,$90.1\,-\,\%$,$\ldots$,$99.9\,-\,\%$

The minimum of the free energy curve is the equilibrium condition. Recall that since this is a minimum, it's slope is zero. Which is why this corresponds to the zero crossing of the earlier graph.
3. Using values from your textbook calculate $\Delta S^\circ$ and $\Delta G^\circ$ for the following reactions:

a. $\text{CO}_2 (g) + \text{H}_2 (g) \rightarrow \text{CO} + \text{H}_2\text{O} (g)$

$$\Delta S^\circ = \left[ (1\text{-mole}) \cdot \left( \frac{197.674 \text{ joule}}{\text{K mole}} \right) + (1\text{-mole}) \cdot \left( \frac{188.825 \text{ joule}}{\text{K mole}} \right) \right] \ldots$$

$$\Delta G^\circ = \left[ (1\text{-mole}) \cdot \left( -137.168 \frac{\text{kJ}}{\text{mole}} \right) + (1\text{-mole}) \cdot \left( -228.572 \frac{\text{kJ}}{\text{mole}} \right) \right] \ldots$$

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

$$\Delta G_{\text{rxn}} = 28.619 \text{ kJ}$$

b. $4 \text{ CO}_2 (g) + 2 \text{ H}_2\text{O} (g) \rightarrow 2 \text{ C}_2\text{H}_2 (g) + 5 \text{ O}_2 (g)$

$$\Delta S^\circ = \left[ (2\text{-mole}) \cdot \left( \frac{200.94 \text{ joule}}{\text{K mole}} \right) + (5\text{-mole}) \cdot \left( \frac{205.138 \text{ joule}}{\text{K mole}} \right) \right] \ldots$$

$$\Delta G^\circ = \left[ (2\text{-mole}) \cdot \left( -139.359 \frac{\text{kJ}}{\text{mole}} \right) + (5\text{-mole}) \cdot \left( 0 \frac{\text{kJ}}{\text{mole}} \right) \right] \ldots$$

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

$$\Delta G_{\text{rxn}} = 2.453 \times 10^3 \text{ kJ}$$