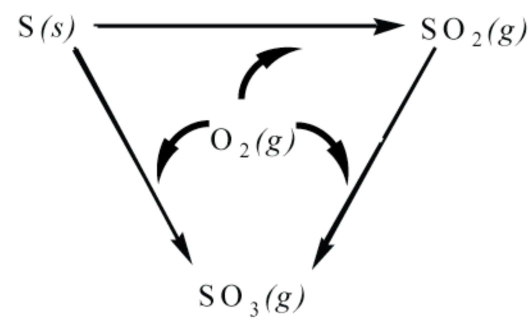
Thermodynamics of the Environmental Production of SO_3

The burning of coal that contains sulfur is one of several contributing factors to acid rain. When sulfur reacts with oxygen it forms $SO_3(g)$, which then dissolves in atmospheric moisture producing sulfuric acid, H_2SO_4. As shown below, there are two pathways by which this might occur. In Pathway I the conversion occurs in two steps:



Rxn Ia: $S(s) + O_2(g) \rightarrow SO_2(g)$

Rxn Ib: $SO_2(g) + 1/2O_2(g) \rightarrow SO_3(g)$

whereas Pathway II consists of a single step:

Rxn II: $S(s) + 3/2O_2(g) \rightarrow SO_3(g)$

The goal of this worksheet is to consider the thermodynamics of these two pathways and to explain why the reaction always proceeds by Pathway I (reactions Ia and Ib) and never by Pathway II.

Thermodynamic values for the compounds involved in these reactions are gathered here:

Compound	ΔH^o_f (kJ/mol$_{rxn}$)	ΔG^o_f (kJ/mol$_{rxn}$)	S^o (J/mol$_{rxn}$·K)
$S(s)$	0	0	31.80
$O_2(g)$	0	0	205.138
$SO_2(g)$	-296.830	-300.194	248.22
$SO_3(g)$	-395.72	-371.06	256.76

Begin by calculating the following thermodynamic values for each reaction:

Reaction	ΔH^o (kJ/mol$_{rxn}$)	ΔG^o (kJ/mol$_{rxn}$)	ΔS^o (J/mol$_{rxn}$·K)
Rxn Ia: $S(s) + O_2(g) \rightarrow SO_2(g)$	-296.83	-300.194	11.282
Rxn Ib: $SO_2(g) + 1/2O_2(g) \rightarrow SO_3(g)$	-98.89	-70.866	-94.029
Rxn II: $S(s) + 3/2O_2(g) \rightarrow SO_3(g)$	-395.72	-371.06	-82.747

Is conservation of energy obeyed for this system of reactions? Explain your reasoning.

Yes. Conservation of energy requires that the ΔH^o, ΔG^o and ΔS^o for two pathways be the same. Adding together values for Reactions Ia and Ib gives the result for Reaction II, confirming the conservation of energy.

When comparing the two pathways, we need to consider reactions Ia and II only. Predict how the favorability of reactions Ia and II will be affected by temperature. That is, will each reaction become more favorable or less favorable at higher temperatures? Explain your reasoning.

For Rxn Ia: $\Delta H^o < 0$ and $\Delta S^o > 0$; thus the reaction is favorable at all temperatures
For Rxn II: $\Delta H^o < 0$ and $\Delta S^o < 0$; thus the reaction is favorable only at lower temperatures

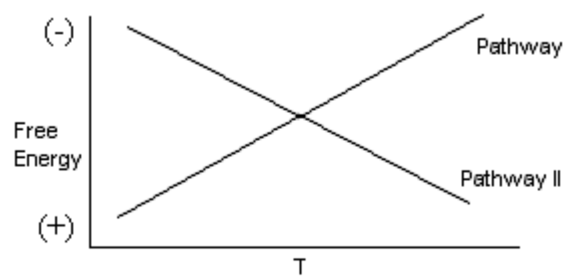
If a reaction become less favorable at higher temperatures, then there must be a critical temperature, T_{crit}, above which the reaction becomes unfavorable. For each of reactions Ia and II, if there is a critical temperature, determine its value.

The critical temperature occurs when $\Delta G^o = 0$; thus, for reaction II, which is the only reaction we need to consider

$$\Delta G^o_{rxn\ II} = 0 = -395.72\ \text{kJ/mol}_{rxn} - T_{crit}\times(-0.082747\ \text{kJ/mol}_{rxn}\cdot\text{K})$$

$$T_{crit} = 4782\ \text{K}$$

Combustion usually occurs at a temperature between 1200 K and 2000 K; thus, the critical temperature for reaction II is insufficient to explain why the reaction proceeds via pathway I. Shown to the right is a sketch of ΔG^o vs. T for the first step of Pathway I and for Pathway II. Explain why these two lines must cross each other. For any two reactions, what must be true if a similar plot is to show parallel lines?



The slope of a plot of ΔG^o vs. T is equivalent to $-\Delta S^o$. Since ΔS^o is positive for reaction Ia and negative for reaction II, the two lines must cross. The only case where two such lines will be parallel is when the reactions have identical values for ΔS^o.

The temperature where the two lines cross is known as T_{cross}. Determine its value and explain its significance in terms of the favorability of Pathway I and Pathway II.

To find T_{cross} we note that at this temperature $\Delta G^o_{rxn\ Ia}$ and $\Delta G^o_{rxn\ II}$ are equal; thus

$$-296.83\ \text{kJ/mol}_{rxn} - T_{cross}\times(0.01182\ \text{kJ/mol}_{rxn}\cdot\text{K}) = -395.72\ \text{kJ/mol}_{rxn} - T_{cross}\times(-0.082747\ \text{kJ/mol}_{rxn}\cdot\text{K})$$

$$98.89\ \text{kJ/mol}_{rxn} = 0.094567\ \text{kJ/mol}_{rxn}\cdot\text{K}$$

$$T_{cross} = 1046\ \text{K}$$

Even at temperatures where Pathway II is the more favorable reaction, the formation of SO_3 still occurs by the two reactions that make up Pathway I. Propose a reason for this observation.

The only reasonable explanation for this observation is that the energy barrier for reaction II must be sufficiently larger that the production of SO_3 follows reaction Ia even though it is the less thermodynamically favorable pathway.