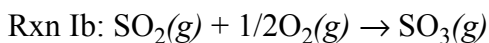
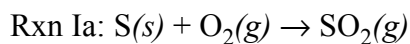
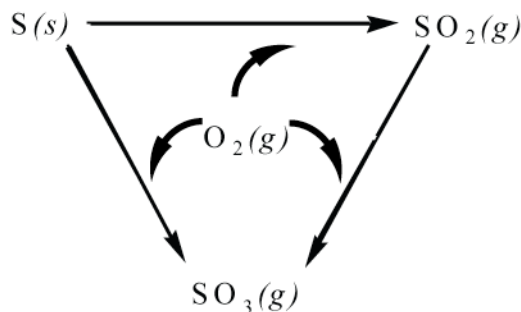
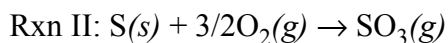


Thermodynamics of the Environmental Production of SO₃

The burning of coal that contains sulfur is one of several contributing factors to acid rain. When sulfur reacts with oxygen it forms SO₃(g), which then dissolves in atmospheric moisture producing sulfuric acid, H₂SO₄. As shown below, there are two pathways by which this might occur. In Pathway I the conversion occurs in two steps:



whereas Pathway II consists of a single step:



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°_f (kJ/mol _{rxn})	ΔG°_f (kJ/mol _{rxn})	S° (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:

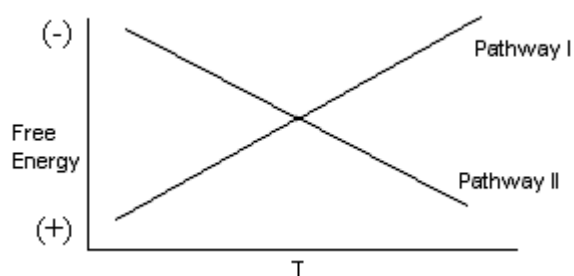
Reaction	ΔH° (kJ/mol _{rxn})	ΔG° (kJ/mol _{rxn})	ΔS° (J/mol _{rxn} ·K)
Rxn Ia: S(s) + O ₂ (g) → SO ₂ (g)			
Rxn Ib: SO ₂ (g) + 1/2O ₂ (g) → SO ₃ (g)			
Rxn II: S(s) + 3/2O ₂ (g) → SO ₃ (g)			

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

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.

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.

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° 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 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.

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.