

Key for Thermodynamics of the Formation of SO₃

The burning of coal that contains sulfur is one of several factors that contribute to acid rain. When sulfur reacts with oxygen it forms SO₃(g), which then dissolves in atmospheric moisture to produce sulfuric acid, H₂SO₄. 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) + O₂(g) → SO₂(g)
- Rxn Ib: SO₂(g) + $\frac{1}{2}$ O₂(g) → SO₃(g)

whereas Pathway II consists of a single step:

- Rxn II: S(s) + $\frac{3}{2}$ O₂(g) → SO₃(g)

The goal of this worksheet is to consider the thermodynamics of these 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° (kJ/mol _{rxn})	ΔG° (kJ/mol _{rxn})	S° (J/K • mol _{rxn})
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:

compound	ΔH° (kJ/mol _{rxn})	ΔG° (kJ/mol _{rxn})	ΔS° (J/K • mol _{rxn})
Rxn Ia: S(s) + O ₂ (g) → SO ₂ (g)	-296.83	-300.194	11.282
Rxn Ib: SO ₂ (g) + $\frac{1}{2}$ O ₂ (g) → SO ₃ (g)	-98.89	-70.866	-94.029
Rxn II: S(s) + $\frac{3}{2}$ O ₂ (g) → SO ₃ (g)	-395.72	-371.060	-82.747

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

Yes. Conservation of energy requires that ΔH° , ΔG° , and ΔS° are the same for both pathways. Adding together the values for reactions Ia and Ib gives the results for reaction II; thus, conservation of energy is obeyed.

When we compare the relative favorability of pathways I and II, we need to consider reactions Ia and II only; after all, if reaction II is more favorable than reaction Ia, then reaction Ib cannot happen. Predict how the favorability of reactions Ia and II are affected by temperature; that is, is each reaction more favorable or less favorable at higher temperatures? Explain your reasoning.

For reaction Ia we have $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$; thus, this reaction is favorable at all temperatures; for reaction II, however, we have $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$, which means this reaction is favorable at lower temperatures only.

If a reaction is favorable at lower temperatures and unfavorable at higher temperatures, then there is 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 is the temperature where $\Delta G^\circ = 0$; thus

$$\Delta G_{II}^\circ = 0 = \Delta H_{II}^\circ - T_{crit}\Delta S_{II}^\circ = -395.72\text{kJ/mol}_{\text{rxn}} - T_{crit}(-0.082747\text{kJ/mol}_{\text{rxn}})$$

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

Given that combustion usually occurs at a temperature between 1200 K and 2000 K, is your answer to the previous question sufficient to explain why the reaction proceeds via pathway I instead of pathway II.

No. Below 4782 K both pathways are thermodynamically favorable processes. We do not yet have sufficient information to know which is the more favorable pathway at the temperature of combustion.

Shown below 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?

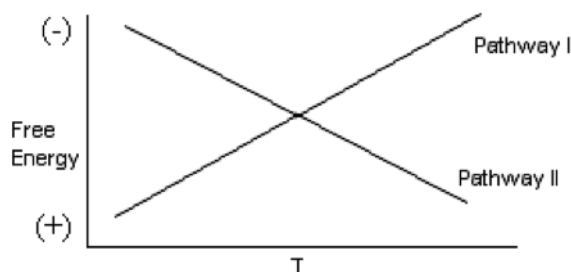


Figure 1: ΔG° as a function of temperature for two pathways leading to the formation of $\text{SO}_3(g)$.

The slope of a plot of ΔG° vs. T is equivalent to ΔS° . Since ΔS° is positive for reaction Ia and negative for reaction II, the two lines must cross. The only case where two such lines are parallel is when the reactions have identical values for ΔS° .

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 set $\Delta G_{Ia}^\circ = \Delta G_{II}^\circ$ and solve; thus

$$\begin{aligned}\Delta H_{Ia}^\circ - T_{cross}\Delta S_{Ia}^\circ &= \Delta H_{II}^\circ - T_{cross}\Delta S_{II}^\circ \\ -296.83\text{kJ/mol}_{\text{rxn}} - T_{cross}(0.01182\text{kJ/mol}_{\text{rxn}}) &= -395.72\text{kJ/mol}_{\text{rxn}} - T_{cross}(-0.082747\text{kJ/mol}_{\text{rxn}}) \\ 98.89\text{kJ/mol}_{\text{rxn}} &= T_{cross}(0.094567\text{kJ/mol}_{\text{rxn}}) \\ T_{cross} &= 1046\text{K}\end{aligned}$$

By the time the combustion gases leave the furnace, their temperature falls below 1000 K; however, the formation of $\text{SO}_3(g)$ still occurs by Pathway I instead of Pathway II. Propose a reason for this observation.

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