

Kirchoff's Law Example

Question: The way we create hydrogen gas is from steam reforming, which is this reaction:
 $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + 3 \text{H}_2(\text{g})$

(note: we get hydrogen from gasoline, essentially)

If I calculate ΔG° at STP, I know that it is positive and thus the reaction will not work. Using Kirchoff's Law, at what temperature does the reaction become favorable at standard pressure? The data table below has all the necessary information:

Material	S° (J/K/mol)	$\Delta_f G^\circ$ (kJ/mol)	$\Delta_f H^\circ$ (kJ/mol)	$C_{p,m}^\circ$ (J/K/mol)
CO(g)	197.7	-137.2	-110.5	29.14
CH ₄ (g)	186.4	-50.7	-74.8	35.31
H ₂ O(g)	188.8	-228.6	-241.8	33.58
H ₂ (g)	130.4	0.0	0.0	28.82

Assume that the heat capacities are pressure independent, and don't worry about the per molar thing, you can just find everything as a per molar quantity.

(Hint: The reaction will become favorable once $\Delta G(T_2)=0$ J/mol, where T_2 is the answer you're looking for. Isn't $\Delta G(T_2)=\Delta H(T_2) - T_2 \times \Delta S(T_2)$?)

Answer: First, note that $\Delta G^\circ = \sum \nu \cdot \Delta_f G^\circ_{\text{products}} - \sum \nu \cdot \Delta_f G^\circ_{\text{reactants}} = -137.2 \text{ kJ/mol} + 3 \times 0 \text{ kJ/mol} - (-228.6 \text{ kJ/mol}) - (-50.7 \text{ kJ/mol}) = +142.1 \text{ kJ/mol}$.

Next, calculate the change in enthalpy of the reaction via:
 $\Delta H^\circ = \sum \nu \cdot \Delta_f H^\circ_{\text{products}} - \sum \nu \cdot \Delta_f H^\circ_{\text{reactants}} = -110.5 \text{ kJ/mol} + 3 \times 0 \text{ kJ/mol} - (-241.8 \text{ kJ/mol}) - (-74.8 \text{ kJ/mol}) = 206.1 \text{ kJ/mol}$. Also, the change in entropy is
 $\Delta S^\circ = \sum \nu \cdot S^\circ_{\text{products}} - \sum \nu \cdot S^\circ_{\text{reactants}} = 197.7 \text{ J/K/mol} + 3 \times 130.4 \text{ J/K/mol} - 188.8 \text{ J/K/mol} - 186.4 \text{ J/K/mol} = 213.7 \text{ J/K/mol}$.

The change in the reaction heat capacity is likewise: $\Delta C_{p,m}^\circ = \sum \nu \cdot C_{p,m}^\circ_{\text{products}} - \sum \nu \cdot C_{p,m}^\circ_{\text{reactants}} = 29.14 \text{ J/K/mol} + 3 \times 28.82 \text{ J/K/mol} - 33.58 \text{ J/K/mol} - 35.31 \text{ J/K/mol} = 46.71 \text{ J/K/mol}$.

Applying Kirchoff's Law for constant heat capacities means that the equation:

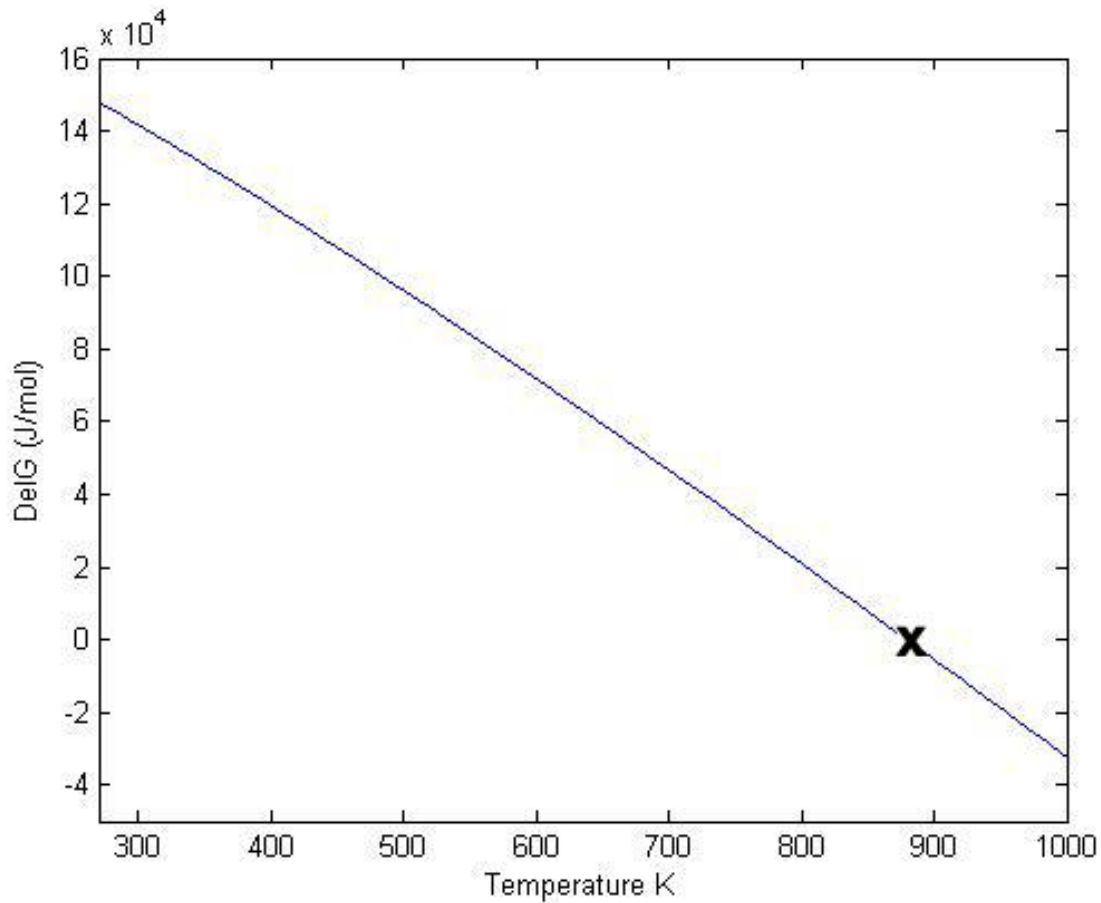
$$\Delta G(T_2) = \Delta H(T_2) - T_2 \cdot \Delta S(T_2) = \Delta H(T_1) + \int_{298.15K}^{T_2} \Delta C_{p,m} \cdot \partial T - T_2 \cdot \left(\Delta S(T_1) + \int_{298.15K}^{T_2} \Delta C_{p,m} \cdot \frac{\partial T}{T} \right) =$$

$$\Delta H(298.15K) + \Delta C_{p,m} \cdot (T_2 - 298.15)K - T_2 \cdot \left(\Delta S(298.15K) + \Delta C_{p,m} \cdot \ln \left(\frac{T_2 K}{298.15K} \right) \right) =$$

$$206,100 \text{ J/mol} + T_2 \times 46.71 \text{ J/K/mol} - 46.71 \text{ J/K/mol} \times 298.15\text{K} - T_2 \times 213.7 \text{ J/K/mol} - T_2 \times 46.71 \text{ J/K/mol} \times \ln(T_2) + T_2 \times 46.71 \text{ J/K/mol} \times \ln(298.15 \text{ K})$$

Simplification gives us: $\Delta G(T_2) = 192,173 \text{ J/mol} + T_2 \times 99.14 \text{ J/K/mol} - T_2 \times 46.71 \text{ J/K/mol} \times \ln(T_2)$.

Now you have to graph the answer to find where $\Delta G(T_2)$ is 0 as so:



Here, you can see that $\Delta G(T_2) = 0 \text{ J/mol}$ when T_2 is $\sim 883 \text{ K}$; at this temperature (or higher) the reaction begins to move forward.