



MAY 11-15, 2020

TOPIC: SECOND LAW OF THERMODYNAMICS

Second Law of Thermodynamics

- The second law of thermodynamics explains the relationship between entropy change and spontaneity of a process.
- It states that for any spontaneous process, there is a net increase in the total entropy of the system and its surroundings.

This net entropy change of the process is represented as ΔS_{univ}

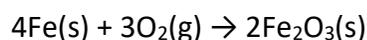
$$\Delta S_{\text{univ}} = [\Delta S_{\text{sys}} + \Delta S_{\text{surr}}] > 0$$

- ✓ Thus, even if ΔS_{sys} is negative, the process can be spontaneous as long as ΔS_{surr} is positive and has a greater magnitude than ΔS_{sys} . If the system is a chemical reaction, ΔS_{sys} is simply the ΔS° of the reaction calculated from the S° value of the reactants and products.
- ✓ Calculating ΔS_{surr} requires recalling the first law of thermodynamics. The entropy change in the surrounding is directly proportional to the enthalpy change of the reaction and inversely proportional to the absolute temperature (in kelvin) of the surroundings.

Mathematically expressed as: $\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{rxn}}}{T}$

Sample problem:

1. Compute for the total entropy change (ΔS_{univ}) in the oxidation of metallic iron into ferric oxide (Fe_2O_3) under standard conditions. Determine the spontaneity of the process at these conditions.



Solution:

First, ΔS° of the reaction is obtained from the S° values of the reactant and products.

Substance	Fe(s)	O ₂ (g)	Fe ₂ O ₃ (s)
S°(J/mol.K)	27.3	205.0	87.4

$$\begin{aligned}\Delta S_{\text{sys}} = \Delta S^\circ &= [2 S^\circ(\text{Fe}_2\text{O}_3) - [4 S^\circ(\text{Fe}) + 3 S^\circ(\text{O}_2)]] \\ &= [(2 \text{ mol})(87.4 \text{ J/mol.K})] - [(4 \text{ mol})(27.3 \text{ J/mol.K}) + (3 \text{ mol})(205.0 \text{ J/mol.K})] \\ &= \mathbf{-595.5 \text{ J/K}}\end{aligned}$$

The $\Delta H^\circ_{\text{rxn}}$ is calculated from the standard molar enthalpies of formation (ΔH°_f) of the reactants and products. Since ΔH°_f to the elemental substances is zero and that for Fe_2O_3 is -824.2 kJ/mol ,

$$\Delta H^\circ_{\text{rxn}} = 2\Delta H^\circ_f(\text{Fe}_2\text{O}_3) = (2 \text{ mol})(-824.2 \text{ kJ/mol}) = -1648.4 \text{ kJ}$$

Therefore, at 25°C (298.15K),

$$\Delta S_{\text{surr}} = -\Delta H^\circ_{\text{rxn}}/T = \frac{-(-1648400 \text{ J})}{298.15 \text{ K}} = \mathbf{5528.8 \text{ J/K}}$$

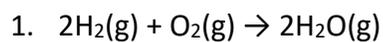
To get the total entropy of the process (ΔS_{univ})

$$\begin{aligned}\Delta S_{\text{univ}} &= [\Delta S_{\text{sys}} + \Delta S_{\text{surr}}] \\ &= -595.5 \text{ J/K} + 5528.8 \text{ J/K} \\ &= \mathbf{4979.3 \text{ J/K}}\end{aligned}$$

The change of entropy in the reaction is negative, but the entropy change in the surroundings is large enough such that the total entropy of the process is positive. This indicates that the oxidation of iron is a spontaneous process at standard conditions.

To Do List

I. Calculate the ΔS° for each given reaction. Copy and answer in a 1 whole sheet of paper.

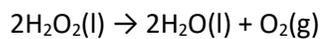


Substance	$\text{H}_2(\text{g})$	$\text{O}_2(\text{g})$	$\text{H}_2\text{O}(\text{g})$
$S^\circ(\text{J/mol.K})$	130.6	205.0	188.7



Substance	$\text{Ca}_3(\text{PO}_4)_2$	Ca^{2+}	PO_4^{3-}
$S^\circ(\text{J/mol.K})$	241.0	-53.1	-222.0

3. Calculate the total entropy change for the decomposition of hydrogen peroxide (H_2O_2). Is the reaction spontaneous or not?



Substance	$\text{H}_2\text{O}_2(\text{l})$	$\text{H}_2\text{O}(\text{l})$	$\text{O}_2(\text{g})$
$S^\circ(\text{J/mol.K})$	109.6	69.9	205.0
$\Delta H_f^\circ(\text{kJ/mol})$	-187.7	-285.8	0