

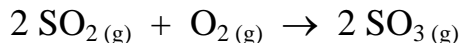
AP CHEMISTRY

TOPIC 9: THERMODYNAMICS, PART C, EXAMPLES, PART II

Day 110:

- Bond Energy
- Third Law of Thermodynamics
- Gibbs Free Energy

Example #1: Calculate the entropy change for the reaction shown below (assume the reaction takes place at 25 °C).



The standard molar entropy values for the substances in the reaction are in the table:

	$\text{J mol}^{-1} \text{K}^{-1}$
$\text{SO}_2(\text{g})$	248.1
$\text{SO}_3(\text{g})$	256.7
$\text{O}_2(\text{g})$	205.0

$$\Delta S^\circ = \sum \Delta S^\circ(\text{products}) - \sum \Delta S^\circ(\text{reactants})$$

$$\Delta S^\circ = [2 \Delta S^\circ(\text{SO}_3)] - [2 \Delta S^\circ(\text{SO}_2) + 3 \Delta S^\circ(\text{O}_2)]$$

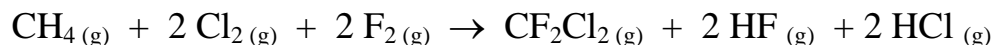
$$\Delta S^\circ = \left[2 \left(\frac{256.7 \text{ J}}{\text{mol} \cdot \text{K}} \right) \right] - \left[2 \left(\frac{248.1 \text{ J}}{\text{mol} \cdot \text{K}} \right) + \left(\frac{205.0 \text{ J}}{\text{mol} \cdot \text{K}} \right) \right] = -187.8 \text{ J mol}^{-1} \text{K}^{-1}$$

Average Bond Energies (kJ/mol)							
Single Bonds				Multiple Bonds			
H—H	432	N—H	391	I—I	149	C=C	614
H—F	565	N—N	160	I—Cl	208	C≡C	839
H—Cl	427	N—F	272	I—Br	175	O=O	495
H—Br	363	N—Cl	200	S—H	347	C=O*	745
H—I	295	N—Br	243	S—F	327	C≡O	1072
		N—O	201	S—Cl	253	N=O	607
C—H	413	O—H	467	S—Br	218	N=N	418
C—C	347	O—O	146	S—S	266	N≡N	941
C—N	305	O—F	190			C≡N	891
C—O	358	O—Cl	203			C=N	615
C—F	485	O—I	234	Si—Si	340		
C—Cl	339			Si—H	393		
C—Br	276	F—F	154	Si—C	360		
C—I	240	F—Cl	253	Si—O	452		
C—S	259	F—Br	237				
		Cl—Cl	239				
		Cl—Br	218				
		Br—Br	193				

*C=O(CO₂) = 799

Example #2:

Using the bond energies (from the table) calculate the ΔH for the reaction of methane with chlorine and fluorine to generate Freon-12 (CF_2Cl_2)



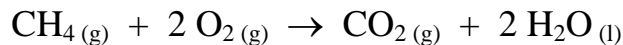
$$\Delta H_{B.E.}^\circ = \sum \text{Bond energies of bonds broken (Reactants)} - \sum \text{Bond energies of bonds formed (Products)}$$

$$\Delta H_{B.E.} = \sum_{\text{Reactants}} - \sum_{\text{Products}}$$

$$\Delta H_{B.E.} = \left[4 \left(\frac{413 \text{ kJ}}{\text{mol}} \right) + 2 \left(\frac{239 \text{ kJ}}{\text{mol}} \right) + 2 \left(\frac{154 \text{ kJ}}{\text{mol}} \right) \right] - \left[\left[2 \left(\frac{485 \text{ kJ}}{\text{mol}} \right) + 2 \left(\frac{339 \text{ kJ}}{\text{mol}} \right) \right] + 2 \left(\frac{565 \text{ kJ}}{\text{mol}} \right) + 2 \left(\frac{427 \text{ kJ}}{\text{mol}} \right) \right] = -1194 \text{ kJ mol}^{-1}$$

Example #3:

Calculate the standard free energy change for the complete combustion of methane, CH₄, at 25 °C.



compound	ΔG^0 (kJ mol ⁻¹)
O ₂ (g)	0
H ₂ O(l)	-237.2
CO ₂ (g)	-394.4
CH ₄ (g)	-50.8

ANSWER:

$$\Delta G^0 = \sum \Delta G^0(\text{products}) - \sum \Delta G^0(\text{reactants})$$

$$\Delta G^0 = [\Delta G^0(\text{CO}_2) + 2 \Delta G^0(\text{H}_2\text{O})] - [\Delta G^0(\text{CH}_4) + 2 \Delta G^0(\text{O}_2)]$$

$$\Delta G^0 = \left[\left(\frac{-394.4 \text{ kJ}}{\text{mol}} \right) + 2 \left(\frac{-237.2 \text{ kJ}}{\text{mol}} \right) \right] - \left[\left(\frac{-50.8 \text{ kJ}}{\text{mol}} \right) + 2 \left(\frac{0 \text{ kJ}}{\text{mol}} \right) \right] = -818 \text{ kJ mol}^{-1}$$

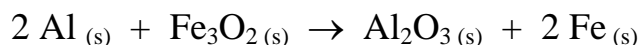
$$\Delta G^0 < 0, \quad \text{The reaction is spontaneous.}$$

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The reaction is spontaneous.

Example #4: You try it...

Calculate the ΔG^0 , for the reaction of aluminum with iron(III) oxide.



compound	ΔG^0 (kJ mol ⁻¹)
Fe ₃ O ₂ (s)	-740.98
Al ₂ O ₃ (s)	-1576.5

ANSWER:

$$\Delta G^0 = \sum \Delta G^0(\text{products}) - \sum \Delta G^0(\text{reactants})$$

$$\Delta G^0 = [\Delta G^0(\text{CO}_2) + 2 \Delta G^0(\text{H}_2\text{O})] - [\Delta G^0(\text{CH}_4) + 2 \Delta G^0(\text{O}_2)]$$

$$\Delta G^0 = \left[\left(\frac{-1576.5 \text{ kJ}}{\text{mol}} \right) + 2 \left(\frac{0 \text{ kJ}}{\text{mol}} \right) \right] - \left[\left(\frac{-740.98 \text{ kJ}}{\text{mol}} \right) + 2 \left(\frac{0 \text{ kJ}}{\text{mol}} \right) \right] = -835.5 \text{ kJ mol}^{-1}$$

$$\Delta G^0 < 0$$

The reaction is spontaneous.