AP CHEMISTRY

TOPIC 9: THERMODYNAMICS, PART C, Day 110:

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

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1. Using the bond energies (from the table on the examples, part II) calculate the ΔH for the reactions: You WILL NEED TO DRAW the Lewis Structures to answer these correctly.

a) $H_{2\,(g)} + Cl_{2\,(g)} \rightarrow 2\ HCl_{(g)}$

$$\boldsymbol{H-H \ + \ Cl-Cl \ \rightarrow 2\ H-Cl}$$

$\Delta H^{0}_{B.E.}$ = Σ Bond energies of bonds broken (Reactants) - Σ Bond energies of bonds formed (Products)

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

$$\Delta H_{B.E.} = \left[\left(\frac{432\ kJ}{mol}\right)+\left(\frac{239\ kJ}{mol}\right)\right]-\left[2\left(\frac{427\ kJ}{mol}\right)\right] = -183\ kJ\ mol^{-1}$$

b) $CH_{4\,(g)} + 2\ O_{2\,(g)} \rightarrow 2\ H_2O_{(g)} + CO_{2\,(g)}$

$$\boldsymbol{4\ C-H \ + 2\ O=O \ \rightarrow \ 4\ O-H \ + \ 2\ C=O}$$

On the product side: 4 O – H, because there are 4 hydrogen atoms which form 4 single bonds to the oxygens. Also, there are two double bonds in the carbon dioxide molecule.

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

$$\Delta H_{B.E.} = \left[4\left(\frac{413\ kJ}{mol}\right)+2\left(\frac{495\ kJ}{mol}\right)\right]-\left[4\left(\frac{467\ kJ}{mol}\right)+2\left(\frac{745\ kJ}{mol}\right)\right] = -716\ kJ\ mol^{-1}$$

2. Calculate the entropy change, ΔS^{0}, for the reaction shown below.

$$2\ H_{2\,(g)} + O_{2\,(g)} \rightarrow 2\ H_2O_{(l)}$$

compound	ΔS^{0} (J mol^{-1} K^{-1})
$O_{2\,(g)}$	205.0
$H_2O_{(l)}$	188.8
$H_{2\,(g)}$	130.6

ANSWER:

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

$$\Delta S^{0} = [\ 2\ \Delta S^{0}\,(H_2O)\ ] - [\ 2\ \Delta S^{0}\,(H_2) + \Delta S^{0}\,(O_2)\ ]$$

$$\Delta S^{0} = \left[2\left(\frac{188.8\ J}{mol\cdot K}\right)\right]-\left[2\left(\frac{130.6\ J}{mol\cdot K}\right)+\left(\frac{205.0\ J}{mol\cdot K}\right)\right] = -88.6\ J\ mol^{-1}K^{-1}$$

3. Calculate the entropy change, ΔS^0, for the reaction shown below.

$$Al_2O_{3\,(s)} + 3\,H_{2\,(g)} \rightarrow 2\,Al_{\,(s)} + 3\,H_2O_{\,(g)}$$

compound	ΔS^0 (J mol^{-1} K^{-1})
$Al_2O_{3\,(s)}$	51.0
$H_2O_{\,(g)}$	189.0
$H_{2\,(g)}$	130.6
$Al_{\,(s)}$	28.0

ANSWER:

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

$$\Delta S^0 = [\, 2\,\Delta S^0(\,Al\,) + 3\,\Delta S^0(\,H_2O\,)\,] - [\,\Delta S^0(\,Al_2O_3\,) + 3\,\Delta S^0(\,H_2\,)\,]$$

$$\Delta S^0 = \left[2\left(\frac{28.0\ J}{mol\cdot K}\right)+3\left(\frac{189.0\ J}{mol\cdot K}\right)\right]-\left[\left(\frac{51.0\ J}{mol\cdot K}\right)+3\left(\frac{130.6\ J}{mol\cdot K}\right)\right] = 180.2\ J\ mol^{-1}K^{-1}$$

4. Calculate the standard free energy change, ΔG^0, for the complete combustion of methanol, $CH_3OH_{\,(g)}$, at 25 ^{0}C.

$$2\,CH_3OH_{\,(g)} + 3\,O_{2\,(g)} \rightarrow 2\,CO_{2\,(g)} + 4\,H_2O_{\,(g)}$$

compound	ΔG^0 (kJ mol^{-1})
$O_{2\,(g)}$	0
$H_2O_{\,(g)}$	-229.4
$CO_{2\,(g)}$	-394.4
$CH_3OH_{\,(g)}$	- 163.2

ANSWER:

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

$$\Delta G^0 = [\, 2\,\Delta G^0(\,CO_2\,) + 4\,\Delta G^0(\,H_2O\,)\,] - [\, 2\,\Delta G^0(\,CH_3OH\,) + 3\,\Delta G^0(\,O_2\,)\,]$$

$$\Delta G^0 = \left[2\left(\frac{-394.4\ kJ}{mol}\right)+4\left(\frac{-229.4\ kJ}{mol}\right)\right]-\left[2\left(\frac{-163.2\ kJ}{mol}\right)+3\left(\frac{0\ kJ}{mol}\right)\right] = -1380\ kJ\ mol^{-1}$$

$\Delta G^0 < 0$, ***The reaction is spontaneous.***

5. Calculate the standard free energy change, ΔG^0, for the following reaction below, at 25 ^{0}C. Also, is this reaction spontaneous?

$$2\,Al_{\,(g)} + 3\,H_2O_{\,(g)} \rightarrow Al_2O_{3\,(g)} + 3\,H_{2\,(g)}$$

compound	ΔG^0 (kJ mol^{-1})
$Al_2O_{3\,(g)}$	-159.0
$H_2O_{\,(g)}$	-228.6
$H_{2\,(g)}$	0
$Al_{\,(g)}$	289.4

ANSWER:

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

$$\Delta G^0 = [\,\Delta G^0(\,Al_2O_3\,) + 3\,\Delta G^0(\,H_2\,)\,] - [\, 2\,\Delta G^0(\,Al\,) + 3\,\Delta G^0(\,H_2O\,)\,]$$

$$\Delta G^0 = \left[\left(\frac{-159.0\ kJ}{mol}\right)+3\left(\frac{0\ kJ}{mol}\right)\right]-\left[2\left(\frac{289.4\ kJ}{mol}\right)+3\left(\frac{-228.6\ kJ}{mol}\right)\right] = -52.0\ kJ\ mol^{-1}$$

$\Delta G^0 < 0$, ***The reaction is spontaneous.***