

Section 74 – Gibbs Energy

74-1. What is the difference between ΔG and ΔG° for a chemical change?

Solution

ΔG : the (Gibbs) free energy change for any reaction under any set of conditions. ΔG° : the (Gibbs) free energy change for a reaction in which the reagents and products are in their standard states (1 bar or 1 atm for gases, 1 M for solutions) at a specified temperature.

74-2. A reaction has $\Delta H^\circ = 100 \text{ kJ/mol}$ and $\Delta S^\circ = 100 \text{ J/molK}$. Is the reaction spontaneous at room temperature? If not, under what temperature conditions will it become spontaneous?

Solution

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$\Delta G^\circ = 100 - 298.15 \times 1000 \frac{\text{J}}{\text{mol} \cdot \text{K}} \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) = 70.2 \text{ kJ/mol}$$

The $\Delta G^\circ > 0$, so the reaction is nonspontaneous at room temperature.

$$\Delta G = \Delta H - T\Delta S$$

$$0 = 100 - T \left[100 \frac{\text{J}}{\text{mol} \cdot \text{K}} \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) \right]$$

$$T = 1000 \text{ K}$$

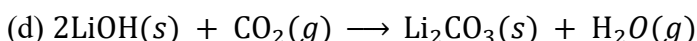
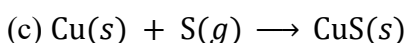
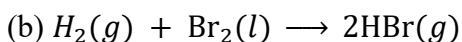
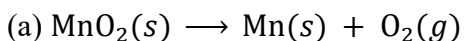
Above 1000 K, ΔG will become negative, and the reaction will become spontaneous.

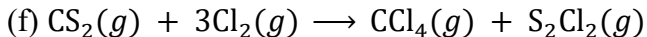
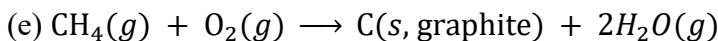
74-3. Explain what happens as a reaction starts with $\Delta G < 0$ (negative) and reaches the point where $\Delta G = 0$.

Solution

The reaction starts with $Q < K$ as the reaction proceeds, and Q increases until equilibrium is reached (where $Q = K$).

74-4. Use the standard free energy of formation data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.





Solution

(a) $\Delta G^\circ = \sum \nu \Delta G_f^\circ(\text{products}) - \sum \nu \Delta G_f^\circ(\text{reactants})$

$$\Delta G^\circ = [1 \text{ mol}(0 \text{ kJ/mol}) + 1 \text{ mol}(0 \text{ kJ/mol})] - [1 \text{ mol}(-465.1 \text{ kJ/mol})] = 465.1$$

nonspontaneous

(b) $\Delta G^\circ = \sum \nu \Delta G_f^\circ(\text{products}) - \sum \nu \Delta G_f^\circ(\text{reactants})$

$$\Delta G^\circ = [2 \text{ mol}(-53.43 \text{ kJ/mol})] - [1 \text{ mol}(0 \text{ kJ/mol}) + 1 \text{ mol}(0 \text{ kJ/mol})] = -106.86 \text{ kJ}$$

spontaneous

(c) $\Delta G^\circ = \sum \nu \Delta G_f^\circ(\text{products}) - \sum \nu \Delta G_f^\circ(\text{reactants})$

$$\Delta G^\circ = [1 \text{ mol}(-53.6 \text{ kJ/mol})] - [1 \text{ mol}(0 \text{ kJ/mol}) + 1 \text{ mol}(238.25 \text{ kJ/mol})] = -291.9 \text{ kJ}$$

spontaneous

(d) $\Delta G^\circ = \sum \nu \Delta G_f^\circ(\text{products}) - \sum \nu \Delta G_f^\circ(\text{reactants})$

$$\Delta G^\circ = [1 \text{ mol}(-1132.19 \text{ kJ/mol}) + 1 \text{ mol}(-228.59 \text{ kJ/mol})] - [2 \text{ mol}(-441.5 \text{ kJ/mol}) + 1 \text{ mol}(-394.36 \text{ kJ/mol})] = -83.4 \text{ kJ}$$

spontaneous

(e) $\Delta G^\circ = \sum \nu \Delta G_f^\circ(\text{products}) - \sum \nu \Delta G_f^\circ(\text{reactants})$

$$\Delta G^\circ = [1 \text{ mol}(0 \text{ kJ/mol}) + 2 \text{ mol}(-228.59 \text{ kJ/mol})] - [1 \text{ mol}(-50.5 \text{ kJ/mol}) + 1 \text{ mol}(0 \text{ kJ/mol})] = -406.7 \text{ kJ}$$

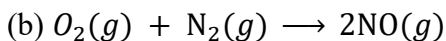
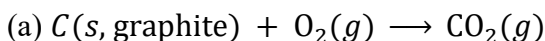
spontaneous

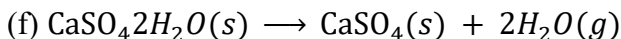
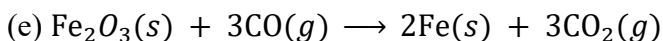
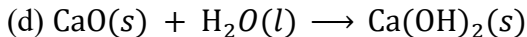
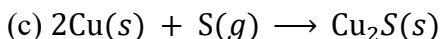
(f) $\Delta G^\circ = \sum \nu \Delta G_f^\circ(\text{products}) - \sum \nu \Delta G_f^\circ(\text{reactants})$

$$\Delta G^\circ = [1 \text{ mol}(-58.2 \text{ kJ/mol}) + 1 \text{ mol}(-29.25 \text{ kJ/mol})] - [1 \text{ mol}(66.8 \text{ kJ/mol}) + 3 \text{ mol}(0 \text{ kJ/mol})] = -154.3 \text{ kJ}$$

spontaneous

74-5. Use the standard free energy data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.





Solution

(a) $\Delta G^\circ = \sum \nu \Delta G_f^\circ(\text{products}) - \sum \nu \Delta G_f^\circ(\text{reactants})$

$$\Delta G^\circ = [1 \text{ mol}(-394.36 \text{ kJ/mol})] - [1 \text{ mol}(0 \text{ kJ/mol}) + 1 \text{ mol}(0 \text{ kJ/mol})] = -394.36 \text{ kJ} \quad \text{spontaneous}$$

(b) $\Delta G^\circ = \sum \nu \Delta G_f^\circ(\text{products}) - \sum \nu \Delta G_f^\circ(\text{reactants})$

$$\Delta G^\circ = [2 \text{ mol}(87.6 \text{ kJ/mol})] - [1 \text{ mol}(0 \text{ kJ/mol}) + 1 \text{ mol}(0 \text{ kJ/mol})] = 175.2 \text{ kJ} \quad \text{nonspontaneous}$$

(c) $\Delta G^\circ = \sum \nu \Delta G_f^\circ(\text{products}) - \sum \nu \Delta G_f^\circ(\text{reactants})$

$$\Delta G^\circ = [1 \text{ mol}(-86.2 \text{ kJ/mol})] - [2 \text{ mol}(0 \text{ kJ/mol}) + 1 \text{ mol}(238.25 \text{ kJ/mol})] = -324.4 \text{ kJ}$$

spontaneous

(d) $\Delta G^\circ = \sum \nu \Delta G_f^\circ(\text{products}) - \sum \nu \Delta G_f^\circ(\text{reactants})$

$$\Delta G^\circ = [1 \text{ mol}(-897.5 \text{ kJ/mol})] - [1 \text{ mol}(-603.3 \text{ kJ/mol}) + 1 \text{ mol}(-237.1 \text{ kJ/mol})] = -57.1 \text{ kJ}$$

spontaneous

(e) $\Delta G^\circ = \sum \nu \Delta G_f^\circ(\text{products}) - \sum \nu \Delta G_f^\circ(\text{reactants})$

$$\Delta G^\circ = [2 \text{ mol}(0 \text{ kJ/mol}) + 3 \text{ mol}(-394.36 \text{ kJ/mol})] - [1 \text{ mol}(-742.2 \text{ kJ/mol}) + 3 \text{ mol}(-137.15 \text{ kJ/mol})] = -29.4 \text{ kJ}$$

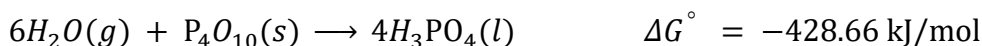
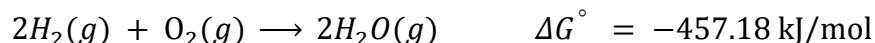
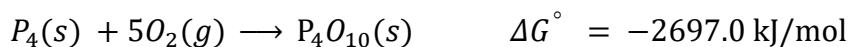
spontaneous

(f) $\Delta G^\circ = \sum \nu \Delta G_f^\circ(\text{products}) - \sum \nu \Delta G_f^\circ(\text{reactants})$

$$\Delta G^\circ = [1 \text{ mol}(-1322.0 \text{ kJ/mol}) + 2 \text{ mol}(-228.59 \text{ kJ/mol})] - [1 \text{ mol}(-1797.45 \text{ kJ/mol})] = 18.3 \text{ kJ}$$

Nonspontaneous

74-6. Given:

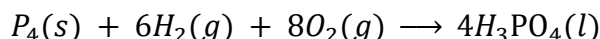


(a) Determine the standard free energy of formation, ΔG_f° , for phosphoric acid.

(b) How does your calculated result compare to the value in Appendix G? Explain.

Solution

(a) The standard free energy of formation is the standard free energy change for $\frac{1}{4}P_4(s) + \frac{3}{2}H_2(g) + 2O_2(g) \longrightarrow H_3PO_4(l)$. We can use a Hess's law-like approach. Note that adding the first reaction plus three times the second reaction plus the third reaction gives, after cancelling terms

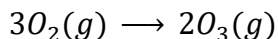


$$\Delta G_{\text{rxn}}^\circ = [(-2697.0) + 3(-457.18) + (-428.66)] \text{ kJ/mol} = -4497.2 \text{ kJ/mol}$$

Dividing this result by four gives the equation of interest. The standard free energy of formation is -1124.3 kJ/mol . (b) The calculation agrees with the value in Appendix G because free energy is a state function (just like the enthalpy and entropy), so its change depends only on the initial and final states, not the path between them.

74-7. Is the formation of ozone ($O_3(g)$) from oxygen ($O_2(g)$) spontaneous at room temperature under standard state conditions?

Solution

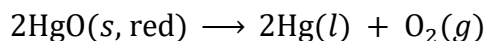


$$\Delta G^\circ = \sum \nu \Delta G_f^\circ(\text{products}) - \sum \nu \Delta G_f^\circ(\text{reactants})$$

$$\Delta G^\circ = [2 \text{ mol}(163.2 \text{ kJ/mol})] - [3 \text{ mol}(0 \text{ kJ/mol})] = 326.4 \text{ kJ};$$

Nonspontaneous

74-8. Consider the decomposition of red mercury(II) oxide under standard state conditions.



(a) Is the decomposition spontaneous under standard state conditions?

(b) Above what temperature does the reaction become spontaneous?

Solution

(a) Using the data in Appendix G, determine ΔG_{298}° :

$$\begin{aligned}\Delta G^\circ &= 2\Delta G_f^\circ(\text{Hg}(l)) + \Delta G_f^\circ(\text{O}_2(g)) - 2\Delta G_f^\circ(\text{HgO}(s, \text{red})) \\ &= \{2(0) + 0 - 2(-58.5)\} \text{ kJ/mol} = 117.0 \text{ kJ/mol}\end{aligned}$$

From its value at 298.15 K, the reaction is nonspontaneous; (b) requires the ratio of the standard enthalpy change to the standard entropy change: $\Delta H^\circ = 2\Delta H_f^\circ(\text{Hg}(l)) +$

$$\begin{aligned}\Delta H_f^\circ(\text{O}_2(g)) - 2\Delta H_f^\circ(\text{HgO}(s, \text{red})) \\ = [2(0) + 0 - 2(-90.83)] \text{ kJ/mol} = 181.66 \text{ kJ/mol} \\ \Delta S^\circ = 2S^\circ(\text{Hg}(l)) + S^\circ(\text{O}_2(g)) - 2S^\circ(\text{HgO}(s, \text{red})) \\ = [2(75.9) + 205.0 - 2(70.29)] \text{ J/K}\cdot\text{mol} = 216.42 \text{ J/K}\cdot\text{mol}\end{aligned}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{181.66 \times 10^3 \text{ J/mol}}{216.42 \text{ J/K}\cdot\text{mol}} = 839 \text{ K} = 566^\circ\text{C}$$

Above 566 °C the process is spontaneous.

74-9. Among other things, an ideal fuel for the control thrusters of a space vehicle should decompose in a spontaneous exothermic reaction when exposed to the appropriate catalyst. Evaluate the following substances under standard state conditions as suitable candidates for fuels.

(a) Ammonia: $2\text{NH}_3(g) \longrightarrow \text{N}_2(g) + 3\text{H}_2(g)$

(b) Diborane: $\text{B}_2\text{H}_6(g) \longrightarrow 2\text{B}(g) + 3\text{H}_2(g)$

(c) Hydrazine: $\text{N}_2\text{H}_4(g) \longrightarrow \text{N}_2(g) + 2\text{H}_2(g)$

(d) Hydrogen peroxide: $\text{H}_2\text{O}_2(l) \longrightarrow \text{H}_2\text{O}(g) + \frac{1}{2}\text{O}_2(g)$

Solution

In each case, determine ΔG° . Suitable fuels will have $\Delta G < 0$ (so that the combustion reaction is favourable) and $\Delta H < 0$ (so that the combustion is exothermic).

$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ(\text{N}_2(g)) + 3\Delta G_f^\circ(\text{H}_2(g)) - 2\Delta G_f^\circ(\text{NH}_3(g)) = 0 + 3(0) - 2(-16.5) = 33 \text{ kJ} \\ \Delta H^\circ &= \Delta H_f^\circ(\text{N}_2(g)) + 3\Delta H_f^\circ(\text{H}_2(g)) - 2\Delta H_f^\circ(\text{NH}_3(g)) = 0 + 3(0) - 2(-46.11) = 92.22 \text{ kJ} \\ \Delta G^\circ &= 2\Delta G_f^\circ(\text{B}(g)) + 3\Delta G_f^\circ(\text{H}_2(g)) - \Delta G_f^\circ(\text{B}_2\text{H}_6(g)) = 2(518.8) + 3(0) - 86.6 = 951 \text{ kJ} \\ \Delta H^\circ &= 2\Delta H_f^\circ(\text{B}(g)) + 3\Delta H_f^\circ(\text{H}_2(g)) - \Delta H_f^\circ(\text{B}_2\text{H}_6(g)) = 2(562.7) + 3(0) - 36 = 1089 \text{ kJ} \\ \Delta G^\circ &= \Delta G_f^\circ(\text{N}_2(g)) + 2\Delta G_f^\circ(\text{H}_2(g)) - \Delta G_f^\circ(\text{N}_2\text{H}_4(g)) = 0 + 2(0) - 159.3 = -159.3 \text{ kJ} \\ \Delta H^\circ &= \Delta H_f^\circ(\text{N}_2(g)) + 2\Delta H_f^\circ(\text{H}_2(g)) - \Delta H_f^\circ(\text{N}_2\text{H}_4(g)) = 0 + 2(0) - 95.4 = -95.4 \text{ kJ}\end{aligned}$$

$$\Delta G^{\circ} = \Delta G_{\text{fH}_2\text{O}(g)}^{\circ} + \frac{1}{2}\Delta G_{\text{fO}_2(g)}^{\circ} - \Delta G_{\text{fH}_2\text{O}_2(l)}^{\circ} = 0 + \frac{1}{2}(0) - 120.4 = -120.4 \text{ kJ}$$

$$\Delta H^{\circ} = \Delta H_{\text{fH}_2\text{O}(g)}^{\circ} + \frac{1}{2}\Delta H_{\text{fO}_2(g)}^{\circ} - \Delta H_{\text{fH}_2\text{O}_2(l)}^{\circ} = 0 + \frac{1}{2}(0) - 187.8 = -187.8 \text{ kJ}$$

(d)

Both reactions (c) and (d) are suitable under the given conditions.

74-10. Determine the standard enthalpy change, entropy change, and free energy change for the conversion of diamond to graphite. Discuss the spontaneity of the conversion with respect to the enthalpy and entropy changes. Explain why diamond spontaneously changing into graphite is not observed.

Solution

The reaction of interest is: $\text{C}(s, \text{diamond}) \rightarrow \text{C}(s, \text{graphite})$

$$\Delta G^{\circ} = \sum \nu \Delta G_f^{\circ}(\text{products}) - \sum \nu \Delta G_f^{\circ}(\text{reactants})$$

$$\Delta H^{\circ} = [1 \text{ mol}(0 \text{ kJ/mol})] - [1 \text{ mol}(1.89 \text{ kJ/mol})] = -1.89 \text{ kJ}$$

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

$$\Delta S^{\circ} = \left[1 \text{ mol} \left(5.74 \frac{\text{J}}{\text{molK}} \right) \right] - \left[1 \text{ mol} \left(2.38 \frac{\text{J}}{\text{molK}} \right) \right] = 3.36 \frac{\text{J}}{\text{molK}}$$

$$\Delta G^{\circ} = \sum \nu \Delta G_f^{\circ}(\text{products}) - \sum \nu \Delta G_f^{\circ}(\text{reactants})$$

$$\Delta G^{\circ} = \left[1 \text{ mol} \left(0 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \right] - \left[1 \text{ mol} \left(2.90 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \right] = -2.90 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

The conversion is spontaneous, $\Delta G^{\circ} < 0$, and is both enthalpy driven (exothermic, $\Delta H^{\circ} < 0$) and entropy driven, $\Delta S^{\circ} > 0$. However, the conversion is so slow that diamonds are effectively very stable (i.e., they are thermodynamically unstable, but kinetically stable).