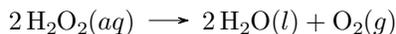


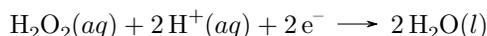
Thermodynamics of Hydrogen Peroxide's Decomposition

Here is a solution to the problem I left you with at the end of today's class, which was to calculate the standard state free energy change, ΔG° , for the reaction

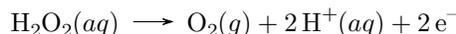


by using the table of standard state reduction potentials, E° , that we discussed in class.

First, we have to divide the reaction up into a reduction reaction and an oxidation reaction that, together, add up to the overall reaction (and these two reactions need to appear in the table if we are to solve the problem) and make note of their potentials; these are the reduction of H_2O_2



which has a reduction potential of 1.776 V, and the oxidation of H_2O_2



which has an oxidation potential of -0.68 V (same magnitude, but opposite sign of the reduction reaction that yields H_2O_2 as a product). If we add together two reactions, then we add together their potentials; thus

$$E_{\text{rxn}}^\circ = 1.776 \text{ V} + (-0.68 \text{ V}) = 1.096 \text{ V}$$

Second, to find the reaction's $\Delta G_{\text{rxn}}^\circ$ we use the equation

$$\Delta G_{\text{rxn}}^\circ = -nFE_{\text{rxn}}^\circ$$

where n is the number of electrons transferred in the overall reaction ($n = 2$ in this case), and F is Faraday's constant of $96,458 \text{ J/V} \cdot \text{mol e}^-$ (or $96.458 \text{ kJ/V} \cdot \text{mol e}^-$); thus

$$\Delta G_{\text{rxn}}^\circ = -(2 \text{ mol e}^- / \text{mol}_{\text{rxn}})(96.458 \text{ kJ/V} \cdot \text{mol e}^-)(1.096 \text{ V}) = -211.4 \text{ kJ/mol}_{\text{rxn}}$$

As a check on this result, we can calculate $\Delta G_{\text{rxn}}^\circ$ using free energies of formation, the values for which are

$$\Delta G_{f,\text{H}_2\text{O}_2(aq)}^\circ = -134.1 \text{ kJ/mol}_{\text{rxn}}$$

$$\Delta G_{f,\text{H}_2\text{O}(l)}^\circ = -237.2 \text{ kJ/mol}_{\text{rxn}}$$

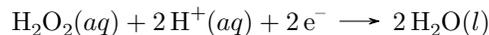
$$\Delta G_{f,\text{O}_2(g)}^\circ = 0 \text{ kJ/mol}_{\text{rxn}}$$

which gives a result

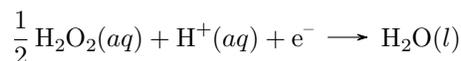
$$\Delta G_{\text{rxn}}^\circ = (2)(-237.2) - (2)(-134.1) = -206.2 \text{ kJ/mol}_{\text{rxn}}$$

that is very close to that found above using potentials.

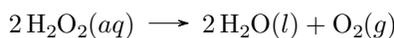
One detail here that is easy to overlook is that we never adjust a standard state reduction potential (or a standard state oxidation potential) for the stoichiometry of the reaction; thus, both



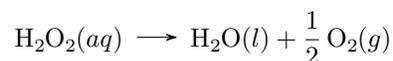
and



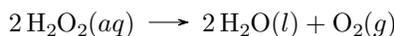
have identical standard state reduction potentials of 1.776 V. This means that the potential for the reaction



and for the reaction



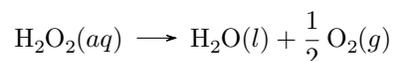
are identical and equal to, as we worked out above, 1.096 V. The values of $\Delta G_{\text{rxn}}^\circ$ are not the same because a reaction's $\Delta G_{\text{rxn}}^\circ$ value depends on how we write the reaction's stoichiometry. We account for this when we convert E_{rxn}° to $\Delta G_{\text{rxn}}^\circ$ by the value of n in $\Delta G_{\text{rxn}}^\circ = -nFE_{\text{rxn}}^\circ$; thus, $\Delta G_{\text{rxn}}^\circ$ for the reaction



for which $n = 2$, is

$$\Delta G_{\text{rxn}}^\circ = -(2 \text{ mol e}^-/\text{mol}_{\text{rxn}})(96.458 \text{ kJ/V} \cdot \text{mol e}^-)(1.096 \text{ V}) = -211.4 \text{ kJ/mol}_{\text{rxn}}$$

and $\Delta G_{\text{rxn}}^\circ$ for the reaction



for which $n = 1$, is

$$\Delta G_{\text{rxn}}^\circ = -(1 \text{ mol e}^-/\text{mol}_{\text{rxn}})(96.458 \text{ kJ/V} \cdot \text{mol e}^-)(1.096 \text{ V}) = -105.7 \text{ kJ/mol}_{\text{rxn}}$$