

17.13: Galvanic Cells and Free Energy

We see in [the section on the Electromotive Force of Galvanic Cells](#) that the emf of a [galvanic cell](#) can tell us whether the cell reaction is [spontaneous](#). In [other sections](#) we show that the free-energy change ΔG of a chemical process also indicates whether that process is spontaneous. It is quite reasonable, then, to expect some relationship between ΔG and E , and indeed one exists.

In [the section on Free Energy](#) we stated that the free-energy change corresponds to the maximum quantity of useful work which can be obtained when a chemical reaction occurs. In other words,

$$\Delta G = -w_{max}$$

where the minus sign is necessary because the free energy decreases as the chemical system does useful work on its surroundings. If we are referring to a [redox reaction](#), that work can be obtained in electrical form by means of an appropriate galvanic cell. It can be measured readily, because when a quantity of charge Q moves through a potential difference ΔV , the work done is given by

$$w = Q\Delta V$$

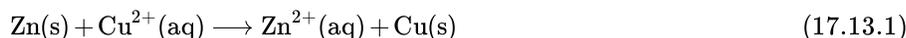
Thus if one coulomb passes through a potential difference of one volt, the work done is

$$w = 1 \text{ C} \times 1 \text{ V} = 1 \text{ A} \cdot \text{s} \times 1 \text{ J A}^{-1} \text{ s}^{-1} = 1 \text{ J}$$

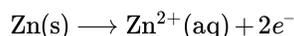
Now suppose we construct a Zn-Cu cell of the type described earlier:



and suppose we make the cell large enough that the concentrations of Cu^{2+} and Zn^{2+} will not change significantly even though 1 mol Zn is oxidized to 1 mol Zn^{2+} according to the cell reaction



If this cell is discharged through a large enough resistance, the potential difference will have its maximum value, namely, the cell emf, E° ; so if we know how much charge is transferred, we can calculate the electrical work done. For the oxidation of 1 mol Zn [that is, for the occurrence of 1 mol of reaction [17.13.1](#)], there must be 2 mol e^- transferred according to the half-equation



Therefore the quantity of electrical charge transferred per mole of reaction is

$$Q_m = 2 \cdot F = 2 \cdot 9 \cdot 649 \times 10^4 \text{ Cmol}^{-1} = 1 \cdot 930 \cdot 10^5 \text{ Cmol}^{-1}$$

(The Faraday constant, F , is the quantity of charge per mole of electrons. It has the value 96,485 C/mol.) The maximum useful work per mole of reaction which the cell can perform while discharging is thus

$$w_{max} = Q_m E^\circ = 2FE^\circ = 2 \cdot 9 \cdot 649 \cdot 10^4 \text{ Cmol}^{-1} \cdot 1 \cdot 10 \text{ V} = 212 \frac{\text{kJ}}{\text{mol}}$$

The standard molar free energy change for the cell reaction is thus

$$\Delta G_m^\circ = -w_{max} = -2FE^\circ = -212 \frac{\text{kJ}}{\text{mol}}$$

A similar argument can be applied to any cell in which the reactants and products are all at their standard concentrations or pressures. If the standard emf of such a cell is E° , while ΔG_m° is the standard molar free energy change for the cell reaction, these two quantities are related by the equation

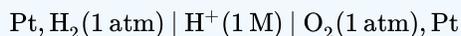
$$\Delta G_m^\circ = -zFE^\circ$$

where z (a dimensionless number) corresponds to the number of moles of electrons transferred per mole of cell reaction. A similar relationship holds even when reactants and products are not at standard concentrations and pressure:

$$\Delta G_m = -zFE$$

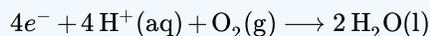
This connection between cell emf and free-energy change provides a means of measuring ΔG_m , directly, rather than by determining ΔH_m , and ΔS_m , and then combining them.

✓ Example 17.13.1 : The emf of a Cell

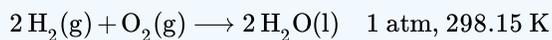


is 1.229 V at 298.15 K. Calculate ΔG_f° for liquid water at this temperature.

Solution: The half-equations for the cell are



so that the cell reaction is



Since there are 4 mol e^- transferred per mol cell reaction, $z = 4$ and

$$\Delta G_m = -zFE = -4 \times \frac{9.649 \times 10^4 \text{C}}{1 \text{ mol}} \times 1.229 \text{V} = -474.3 \frac{\text{kJ}}{\text{mol}}$$

The reaction produces liquid water at standard pressure and the desired temperature, but 1 mol reaction produces 1 mol $2\text{H}_2\text{O}(\text{l})$, that is, 2 mol H_2O . Therefore

$$\Delta G_f^\circ[\text{H}_2\text{O}(\text{l}), 298 \text{ K}] = \frac{1}{2} \Delta G_m = -237.2 \frac{\text{kJ}}{\text{mol}}$$

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