

Units of free energy and electrochemical cell potentials

Notes on General Chemistry

<http://quantum.bu.edu/notes/GeneralChemistry/FreeEnergyUnits.pdf>
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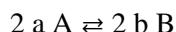
"The devil is in the details."

Units of ΔG for chemical transformations

There is a subtlety about the relation between ΔG and K , namely how ΔG changes when the amounts of reactants and products change. Gibbs free energy

$$G = H - TS$$

is an *extensive quantity*, that is, it depends on how much of the system we have, since H and S are both extensive (T is *intensive*). This means if we double the reactants and products,



then ΔG must also double, but the expression

$$\Delta G = RT \ln(Q/K)$$

found in textbooks does not seem to contain the amounts of reactants and products! In fact it *does* contain these, because the stoichiometric coefficients appear as exponents in Q and K . Thereby, doubling the moles of reactants and products will change Q and K into their square, which will double ΔG . Here is how.

$$\begin{aligned} \Delta G(\text{doubled}) &= RT \ln(Q^2/K^2) \\ &= RT \ln(Q/K)^2 \\ &= 2 RT \ln(Q/K) \\ &= 2 \Delta G(\text{original}) \end{aligned}$$

This result evidently means that

the units of ΔG are energy, not energy per mole, but with the understanding that it is the change in Gibbs free energy per mole of reaction as written.

The question arises, why is this not taken account by the explicit units in the equation for ΔG ? The answer is that the appropriate unit has been omitted. Here is how to see what is going on. The connection between ΔG , Q , and K comes from equalities like

$$a RT \ln(1 \text{ atm} / p_A) = RT \ln(1 \text{ atm} / p_A)^a$$

Now, we know that exponents must be dimensionless, so such an equality means that the exponent a is the *numerical value of the stoichiometric coefficient, without any units*. The units of the stoichiometric coefficient *remain behind, multiplying the gas constant R* . Strictly, therefore, we should make this explicit by writing

$$a R T \ln(1 \text{ atm} / p_A) = \text{mol } R T \ln(1 \text{ atm} / p_A)^{a/\text{mol}}$$

which then leads to the explicitly correct result that

$$\Delta G = \text{mol } R T \ln(Q / K).$$

The problem is, this is never done in textbooks. The bottom line is that when we see the relation $\Delta G = R T \ln(Q / K)$, we just need to understand that (1) exponents are pure numbers, and (2) the units are energy for the reaction, not energy per mole.

Units of electrochemical cell potentials

Proper treatment of mol units in the relation between ΔG , Q , and K carries over into the Nernst equation. Here is how to see this.

The Nernst equation is based on the alternative expressions for free energy change,

$$\Delta G = \text{mol } R T \ln(Q / K)$$

and

$$\Delta G = -n \mathcal{F} \mathcal{E}$$

Setting these equal, and using the special cases of these expressions that

$$\Delta G^\circ = -\text{mol } R T \ln(K)$$

and

$$\Delta G^\circ = -n \mathcal{F} \mathcal{E}^\circ$$

the result is

$$\mathcal{E} = \mathcal{E}^\circ - \frac{\text{mol } R T}{n \mathcal{F}} \ln(Q)$$

This form of the Nernst equation differs from the form in standard textbooks by the explicit mol unit in the numerator of the last term. That this unit must be present can be seen by considering the units in the factor multiplying $\ln(Q)$.

$$\begin{aligned} & \frac{\text{mol } R T}{n \mathcal{F}} \\ &= \frac{\text{mol Joule} / (\text{Kelvin mol}) \text{ Kelvin}}{(\text{mol of electrons}) (\text{Coulomb} / \text{mol of electrons})} \\ &= \frac{\text{Joule}}{\text{Coulomb}} \\ &= \text{Volt} \end{aligned}$$

That is, by having properly accounted for mol units in the expression for free energy, we achieve proper units in each term of the Nernst equation, and so in particular the Q -dependent term of the Nernst equation is an explicitly *intensive* quantity.