Concentration and Activity

Plugging the Right Numbers Into Energy Calculations

(Thanks to Robert Lindquist, whose book* straightened me out on some of these matters.)

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Consider the reaction

2 NADH + $2H^+$ + O_2 --> 2 NAD^+ + 2 H_2O
occurring in aqueous solution at pH 7.6, [NAD^+] = 20.0 mM, [NADH] = 10.0 mM, and oxygen at a partial pressure of 100.0 torr. The free-energy change for this oxidation of NADH by oxygen is

What numbers should you plug in for the concentration terms?

These terms are properly *activities*, not concentrations. To convert each concentration into activity, divide it by its standard concentration. This eliminates all units within the logarithm term, because each quantity is divided by a standard concentration in the same units. Here are the details for each type of reactant and product:

Solutes

For dilute (ideal) solutions, the standard state of the solute is 1.00 M, so its molar (*not millimolar*) concentration EQUALS its activity. So in this calculation, plug in [NAD^+] = 0.0200, and [NADH] = 0.0100.

Gases

The standard state for a gas is a pressure of 1 atm or 760 torr. So in this calculation, plug in $[O_2]$ = 100 torr/760 torr = 0.132.

Hydrogen Ion

The biochemical standard state for hydrogen ion is pH 7, or 10^{-7} M. If the pH is 7.6, $[H^+] = 2.5 \times 10^{-8}$. So in this calculation, plug in [H+] = $(2.5 \times 10^{-8})/(10^{-7}) = 0.251$.

NOTE: The prime ['] on $\Delta G^{0'}$ implies that we are using biochemical standard states rather than conventional thermodynamic standard states. In thermodynamics, the standard state for the hydrogen ion is pH = 0 ($[H^+]$ = 1.00 M).

Water

The standard state for a liquid is the pure liquid, so the standard state of water is pure water, whose concentration is 55.5 M (in a liter, there are 55.5 moles of water, so its concentration is 55.5 mol/L). In dilute aqueous solutions, the concentration of water is very close to 55.5 M. So in this calculation, plug in $[H_2O]$ = 1.00 (which is 55.5 M, the actual concentration, divided by 55.5 M, the standard concentration). (NOTE: In a cell, the total solute concentration is high, so the concentration of water is certainly lower than 55.5 M. Nevertheless, biochemists commonly use 1.00 as the activity of water. (But you gotta love 'em.) Of course, if water is not in the balanced equation, it doesn't matter what the actual $[H_20]$ is.

Calculation:

$$\Delta G = \Delta G^{0'} + 15.3 \text{ kJ/mol.}$$

(For an example of $\Delta G^{0'}$ calculation, see Summary of Energy Calculations.)

Summary

Reaction Component	How To Convert To Activity	Example (Quantity => Activity)
Solute	Convert concentration to molarity. Drop units.	[solute] = 2.1 nM => 2.1 x 10^{-9} M, use 2.1 x 10^{-9}
Gas	Convert gas pressure to atm. Drop units.	$P_{(gas)}$ = 45 kPa => 45 kPa/101.3 kPa/atm = 0.44 M, use 0.44
H^+	Divide molar concentration by 10^{-7} M (for biochemical standard state only). M units cancel out.	pH = 6 => 10^{-6} M/10^{-7} M = 10
H_2O	For dilute solutions, use 1.00. (For concentrated solutions, divide molarity of water by 55.5 M.)	Dilute aqueous solution => 1.00

* *Problems and Solutions to Accompany Rawn: Biochemistry*, Neil Patterson Publishers, 1990, p 157.

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