

Supporting Information

**"How Should I Think About Voltage? What is Overpotential?"
– Establishing an Organic Chemistry Intuition for Electrochemistry**

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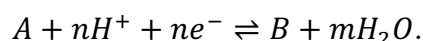
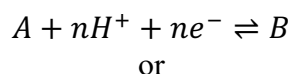
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1. Process for Determining Reduction Potentials from Thermochemical Data

Reduction potentials were primarily calculated from thermochemical data curated by the National Institute of Standards and Technology (NIST).¹ Some values were obtained through review of the literature.²⁻⁴

Below is given the process for determining reduction potentials for a redox couple A/B of the form:



First, calculate the standard free energy of formation ΔG_f° of the reactants and products using equation (1):

$$\Delta G_f^\circ(A) = \Delta H_f^\circ(A) - T \cdot \Delta S_f^\circ(A) \quad (1)$$

where $\Delta H_f^\circ(A)$ is a known, tabulated value and $\Delta S_f^\circ(A)$ is calculated from the known, tabulated value for the compound's molar entropy, $S^\circ(A)$, using equation (2):

$$\Delta S_f^\circ(A) = S^\circ(A) - \sum S^\circ(C, H_2, O_2, N_2, S, \dots) \quad (2)$$

where the latter term is the sum of the molar entropies of the constituent elements in their standard states, each normalized for their stoichiometry in the compound of interest. In cases where the molar entropies are not tabulated, they can be extrapolated from known specific heat vs temperature data (*vide infra*).

Next, calculate the standard free energy of the reaction using equation (3)

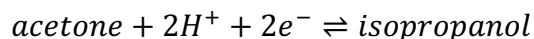
$$\Delta G_{rxn}^\circ = \Delta G_f^\circ(B) - \Delta G_f^\circ(A) \quad (3)$$

Finally, calculate the standard potential E° (V) using equation (4), utilizing the value of ΔG_{rxn}° ($J \cdot mol^{-1}$) obtained from equation (3).

$$E^\circ(vs SHE) = \frac{-\Delta G_{rxn}^\circ}{n \cdot F} \quad (4)$$

2. Worked Example for the Derivation of the Standard Potential for the Acetone/Isopropanol Redox Couple

The balanced equation for the acetone/isopropanol redox couple can be written as follows:



The tabulated thermodynamic values for all relevant species are given in **Table S1**. Note that ΔH_f° and S° values were obtained from NIST database, while ΔS_f° and ΔG_f° values were calculated as described above.

Table S1. Thermodynamic values for all species required for standard potential measurements. ^aValues in italics are exactly zero by definition.

Species	ΔH_f° (kJ mol ⁻¹)	S° (J mol ⁻¹ K ⁻¹)	ΔS_f° (J mol ⁻¹ K ⁻¹)	ΔG_f° (kJ mol ⁻¹)
C(s)	<i>0^a</i>	5.8	<i>0</i>	<i>0</i>
H ₂ (g)	<i>0</i>	130.7	<i>0</i>	<i>0</i>
O ₂ (g)	<i>0</i>	205.2	<i>0</i>	<i>0</i>
acetone(l)	-249.4	200.4	-311.7	-156.5
Isopropanol(l)	-317.0	180.6	-462.2	-179.3

First, calculate the standard enthalpy of formation, ΔS_f° , for acetone and isopropanol (calculations only shown for acetone). Writing equation (2) for acetone gives:

$$\Delta S_f^\circ(\text{acetone}) = S^\circ(\text{acetone}) - [(3 \cdot S_C^\circ) + (3 \cdot S_{\text{H}_2}^\circ) + (0.5 \cdot S_{\text{O}_2}^\circ)]$$

Using the tabulated molar entropy values for acetone and its constituent elements in their standard state, the standard entropy of formation can be calculated:

$$\begin{aligned} \Delta S_f^\circ(\text{acetone}) &= 200.4 - [(3 \cdot 5.8) + (3 \cdot 130.7) + (0.5 \cdot 205.2)] \\ \Delta S_f^\circ(\text{acetone}) &= -311.6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ \Delta S_f^\circ(\text{acetone}) &= -0.3116 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \end{aligned}$$

Next, calculate the standard free energy of formation, ΔG_f° , for acetone and isopropanol (calculation only shown for acetone).

$$\begin{aligned} \Delta G_f^\circ(\text{acetone}) &= \Delta H_f^\circ(\text{acetone}) - T \cdot \Delta S_f^\circ(\text{acetone}) \\ \Delta G_f^\circ(\text{acetone}) &= -249.4 - [298 \cdot (-0.3116)] \\ \Delta G_f^\circ(\text{acetone}) &= -156.5 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

Then, calculate the standard free energy of the reaction, ΔG_{rxn}° , for the acetone/isopropanol redox couple using equation (3):

$$\begin{aligned}\Delta G_{rxn}^{\circ} &= \Delta G_f^{\circ}(\text{isopropanol}) - \Delta G_f^{\circ}(\text{acetone}) \\ \Delta G_{rxn}^{\circ} &= (-179.3) - (-156.5) \\ \Delta G_{rxn}^{\circ} &= -22.8 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

Finally, Calculate the standard potential for the acetone/isopropanol redox couple using the Nernst equation (4):

$$\begin{aligned}E^{\circ} &= \frac{-\Delta G_{rxn}^{\circ}}{n \cdot F} \\ E^{\circ} &= \frac{-(-22.8)}{2 \cdot 96.485} \\ E^{\circ} &= \mathbf{0.118 \text{ V}} \text{ vs SHE}\end{aligned}$$

3. Process for Determining Molar Entropy from Specific Heat and Temperature Data

In cases where the value for the molar entropy for a compound is not known, it can be estimated from specific heat vs. temperature data, should the latter also be available. This can be done by using the relationship between entropy and specific heat capacity, C_p :

$$TdS = C_p dT \quad (5)$$

Equation (5) can be used to find an expression for the change in entropy over a given temperature range:

$$\begin{aligned}dS &= \frac{C_p}{T} dT \\ \int dS &= \int_{T_1}^{T_2} \frac{C_p}{T} dT \\ \Delta S &= \int_{T_1}^{T_2} \frac{C_p}{T} dT\end{aligned}$$

Using an empirical polynomial fit of the heat capacity, we can rewrite the above equation:

$$\Delta S = \int_{T_1}^{T_2} \frac{(AT^3 + BT^2 + CT + D)}{T} dT = \int_{T_1}^{T_2} (AT^2 + BT + C + DT^{-1}) dT$$

The definite integral can be expressed as:

$$\Delta S = \int_{T_1}^{T_2} (AT^2 + BT + C + DT^{-1}) dT = \left[\frac{AT^3}{3} + \frac{BT^2}{2} + CT + D \ln(T) + E \right]_{T_1}^{T_2}$$

$$\Delta S = \left[\frac{AT_2^3}{3} + \frac{BT_2^2}{2} + CT_2 + D\ln(T_2) + E \right] - \left[\frac{AT_1^3}{3} + \frac{BT_1^2}{2} + CT_1 + D\ln(T_1) + E \right]$$

$$\Delta S = \frac{A}{3}(T_2^3 - T_1^3) + \frac{B}{2}(T_2^2 - T_1^2) + C(T_2 - T_1) + D\ln\left(\frac{T_2}{T_1}\right) \quad (6)$$

Therefore, specific heat vs. temperature data can be fit using a cubic polynomial function, which can give values for the parameters A , B , C , and D . Using the Debye theory assumption that in the low temperature limit, $C_p = A_D T^3$, we select a temperature of 10 K as the point where the two C_p models cross over. From this, the value of A_D and ΔS from $T_1 = 0$ K (absolute zero) to $T_2 = 10$ K are determined. Subsequently, the molar change in entropy, ΔS , from $T_1 = 10$ K to $T_2 = 298$ K can be calculated using equation (6). Notice that the overall molar change in entropy from absolute zero to 298 K is equal to the standard molar entropy of the compound (*i.e.*, in this specific case, $\Delta S = S^\circ$) minus the entropy of any phase changes.

Table S2. Specific heat vs temperature data for isopropanol

C_p (J mol ⁻¹ K ⁻¹)	T (K)
35.32	50
46.04	100
57.98	150
68.28	200
83.72	273.15
89.32	298.15

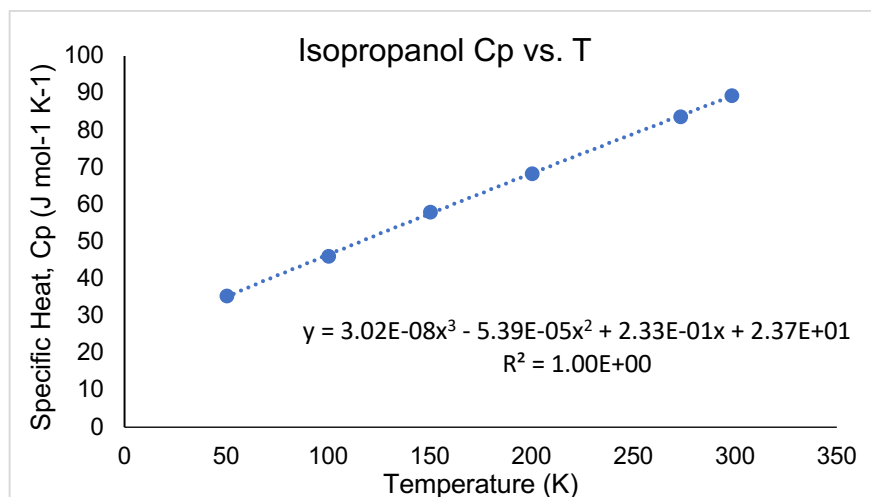


Figure S1. Specific heat vs temperature data for isopropanol with cubic line of best fit.

The line of best fit from **Figure S1.** gives values for A , B , C , and D of $3.0 \cdot 10^{-8}$, $-5.4 \cdot 10^{-5}$, $2.3 \cdot 10^{-1}$, and 23.7, respectively. The C_p at $T = 10$ K is determined using equation (6) and the

values for A , B , C , and D , giving a value of $26 J \cdot mol^{-1} \cdot K^{-1}$. The value for A_D at $T = 10 K$ is subsequently evaluated to be 0.026. The definite integral of $C_p = A_D T^3$ from $T_1 = 0 K$ to $T_2 = 10 K$ gives a corresponding low-temperature entropy of $8.7 J \cdot mol^{-1} \cdot K^{-1}$. The molar change in entropy, ΔS , from $T_1 = 10 K$ to $T_2 = 298 K$ calculated using equation (6) is $145 J \cdot mol^{-1} \cdot K^{-1}$. The value for S^o obtained after summing the above two values and adding the entropy of fusion ($29.2 J \cdot mol^{-1} \cdot K^{-1}$) is $183 J \cdot mol^{-1} \cdot K^{-1}$. This is in close agreement with the literature molar entropy value of $181 J \cdot mol^{-1} \cdot K^{-1}$ for isopropanol. The standard potential values for the acetone/isopropanol couple obtained using the estimated and literature molar entropy values of isopropanol are 0.122 V and 0.118 V vs SHE, respectively. The difference of 4 mV is small compared to the difference in substrate/mediator or substrate/oxidant potentials, validating this method as a way of estimating molar entropy values. This approach was used to derive S^o for acetanilide.

4. Tabulated Potentials for the Oxidants

The potentials of the oxidants listed in Figure 2 are collected with the associated references in 5-10

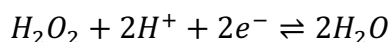
Table S3. Potentials (vs. SHE) for the oxidant half reactions listed in Figure 1. TBHP = *tert*-Butyl hydroperoxide; TEMPO⁺ = 2,2,6,6-tetramethyl-1-oxopiperidinium; TEMPOH₂⁺ = 2,2,6,6-tetramethyl-1-hydroxyl piperidinium; DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; DDH₂Q = 2,3-dichloro-5,6-dicyano-1,4-hydroquinone; BQ = 1,4-benzoquinone; H₂Q = 1,4-hydroquinone. ^aPotential vs. NHE.

Oxidant Reactions	ΔE^o (V)	Reference
$O_2 + 4H^+ + 4e^- \rightleftharpoons H_2O$	1.23	(7)
$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	0.68	
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	1.78	(7)
$O_3 + 2H^+ + 2e^- \rightleftharpoons O_2 + H_2O$	2.08	(7)
$S_2O_8^{2-} + 2H^+ + 2e^- \rightleftharpoons 2SO_4^{2-}$	2.01	(7)
$TBHP + 2H^+ + 2e^- \rightleftharpoons tBuOH + H_2O$	~1.7	(see below)
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	1.507	(7)
$PhIX_2 + 2e^- \rightleftharpoons PhI + 2X^-$	~1.35 ^a	(5), (6)
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{+3} + 7H_2O$	1.36	(7)
$Br_{2(aq)} + 2e^- \rightleftharpoons 2Br^-$	1.09	(7)
$NO_2 + 2H^+ + 2e^- \rightleftharpoons NO + H_2O$	1.05	(8)
$TEMPO^+ + 2H^+ + 2e^- \rightleftharpoons TEMPOH_2^+$	0.91 ^a	(9)
$DDQ + 2H^+ + 2e^- \rightleftharpoons DDH_2Q$	0.89 ^a	(10)
$BQ + 2H^+ + 2e^- \rightleftharpoons H_2Q$	0.64 ^a	(10)
$I_2 + 2e^- \rightleftharpoons 2I^-$	0.54	(7)

5. Estimating the potential of TBHP/*t*-butanol

Though the ΔH_f° of tert-butyl hydroperoxide (TBHP) is tabulated,¹ the molar entropy S° is not known, nor is heat capacity vs temperature data for this compound available. Therefore, estimating S° for TBHP as described above is not feasible. To approximate this value, an assumption can be made that the ΔS_{rxn}° for the TBHP/*t*BuOH+H₂O couple is the same as that for the H₂O₂/H₂O couple. This is a reasonable assumption, since, barring any dramatic solvation effects, the difference in entropy for the two redox couples should be dictated by the 1:2 stoichiometry of sub^{ox} : sub^{red}, as well as the degrees of freedom gained/lost upon replacing an O-O bond with two O-H bonds.

We can write a balanced redox couple for H₂O₂/H₂O and write the corresponding expression for the standard free energy of the reaction:



$$\Delta G_{rxn}^\circ = 2 \cdot \Delta G_f^\circ(H_2O) - \Delta G_f^\circ(H_2O_2) \quad (7)$$

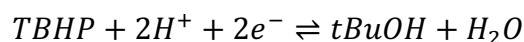
$$\Delta G_{rxn}^\circ = 2 \cdot [\Delta H_f^\circ(H_2O) - T \cdot \Delta S_f^\circ(H_2O)] - [\Delta H_f^\circ(H_2O_2) - T \cdot \Delta S_f^\circ(H_2O_2)] \quad (8)$$

$$\Delta G_{rxn}^\circ = [2 \cdot \Delta H_f^\circ(H_2O) - \Delta H_f^\circ(H_2O_2)] + T \cdot [\Delta S_f^\circ(H_2O_2) - 2 \cdot \Delta S_f^\circ(H_2O)] \quad (9)$$

The standard change in entropy for the H₂O₂/H₂O redox couple can be expressed as:

$$\Delta S_{rxn}^\circ(H_2O_2/H_2O) = \Delta S_f^\circ(H_2O_2) - 2 \cdot \Delta S_f^\circ(H_2O) \quad (10)$$

Similarly, we can write a balanced redox couple for TBHP/*t*BuOH+H₂O and write the corresponding expression for the standard free energy of the reaction:



$$\Delta G_{rxn}^\circ = \Delta G_f^\circ(H_2O) + \Delta G_f^\circ(tBuOH) - \Delta G_f^\circ(TBHP) \quad (11)$$

$$\Delta G_{rxn}^\circ = [\Delta H_f^\circ(H_2O) - T \cdot \Delta S_f^\circ(H_2O)] + [\Delta H_f^\circ(tBuOH) - T \cdot \Delta S_f^\circ(tBuOH)] - [\Delta H_f^\circ(TBHP) - T \cdot \Delta S_f^\circ(TBHP)] \quad (12)$$

$$\Delta G_{rxn}^\circ = [\Delta H_f^\circ(H_2O) + \Delta H_f^\circ(tBuOH) - \Delta H_f^\circ(TBHP)] + T \cdot [\Delta S_f^\circ(TBHP) - \Delta S_f^\circ(H_2O) - \Delta S_f^\circ(tBuOH)] \quad (13)$$

The standard change in entropy for the TBHP/*t*BuOH redox couple can be expressed as:

$$\Delta S_{rxn}^\circ(TBHP/tBuOH) = \Delta S_f^\circ(TBHP) - \Delta S_f^\circ(H_2O) - \Delta S_f^\circ(tBuOH) \quad (14)$$

Based on our assumption that ΔS_{rxn}° for the TBHP/*t*BuOH+H₂O couple is the same as that for the H₂O₂/H₂O couple (using the value for liquid phase H₂O₂), we can write:

$$\Delta S_{rxn}^{\circ}(TBHP/tBuOH) = \Delta S_{rxn}^{\circ}(H_2O_2/H_2O) = \Delta S_f^{\circ}(H_2O_2) - 2 \cdot \Delta S_f^{\circ}(H_2O) \quad (15)$$

Thus, the expression for the standard free energy of the TBHP/tBuOH+H₂O redox couple becomes:

$$\Delta G_{rxn}^{\circ} = [\Delta H_f^{\circ}(H_2O) + \Delta H_f^{\circ}(tBuOH) - \Delta H_f^{\circ}(TBHP)] + T \cdot [\Delta S_f^{\circ}(H_2O_2) - 2 \cdot \Delta S_f^{\circ}(H_2O)] \quad (16)$$

The above free energy is now expressed in terms of known or calculable values.^{1,4} Inserting the above values gives:

$$\Delta G_{rxn}^{\circ} = [(-285.83 \text{ kJ} \cdot \text{mol}^{-1}) + (-359.2 \text{ kJ} \cdot \text{mol}^{-1}) - (-294 \text{ kJ} \cdot \text{mol}^{-1})] + 298 \text{ K} \cdot [(-0.22636 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) - 2 \cdot (-0.163305 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})] \quad (17)$$

$$\Delta G_{rxn}^{\circ} = -321.16 \text{ kJ mol}^{-1} \quad (18)$$

Using the Nernst equation for the 2e⁻/2H⁺ couple, the expression for the standard potential becomes:

$$E^{\circ} = \frac{-\Delta G_{rxn}^{\circ}}{n \cdot F}$$

$$E^{\circ} \sim \frac{-(-321.16) \cdot 1000}{2 \cdot 96.485}$$

$$E^{\circ} \sim 1.7 \text{ V vs SHE}$$

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