Supplemental Information

Thermodynamic Discrimination
between Energy Sources for Chemical Reactions

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Supplemental References
Table S1: Molecule raw thermodynamic parameters. These raw values are used to generate the reaction enthalpies and entropies used in the main text (primarily Figure 6).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\Delta H_f^0$ (kJ/mol)</th>
<th>$S_f^0$ (J/mol.K)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>-393.52</td>
<td>213.79</td>
<td>g</td>
</tr>
<tr>
<td>CO</td>
<td>-110.53</td>
<td>197.66</td>
<td>g</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>-74.6</td>
<td>186.25</td>
<td>g</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-241.83</td>
<td>188.84</td>
<td>g</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-285.83</td>
<td>69.95</td>
<td>ℓ</td>
</tr>
<tr>
<td>MeOH</td>
<td>-205</td>
<td>239.81 c</td>
<td>g</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0</td>
<td>130.68</td>
<td>g</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0</td>
<td>191.61</td>
<td>g</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0</td>
<td>205.15</td>
<td>g</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>-45.9</td>
<td>192.77</td>
<td>g</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>-1675.69</td>
<td>50.92</td>
<td>s</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>5.6</td>
<td>s</td>
</tr>
<tr>
<td>Al</td>
<td>0</td>
<td>28.3</td>
<td>s</td>
</tr>
<tr>
<td>NaCl</td>
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</tr>
<tr>
<td>Cl$_2$</td>
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<td>223.08</td>
<td>g</td>
</tr>
<tr>
<td>NaOH</td>
<td>-425.93</td>
<td>64.46</td>
<td>s</td>
</tr>
<tr>
<td>Propanal</td>
<td>-188.7</td>
<td>304.4</td>
<td>g</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>52.4</td>
<td>219.32</td>
<td>g</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>-84.0</td>
<td>229.1 d</td>
<td>g</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>-20.5</td>
<td>205.77</td>
<td>g</td>
</tr>
<tr>
<td>S</td>
<td>1.85</td>
<td>36.85</td>
<td>ℓ</td>
</tr>
<tr>
<td>S</td>
<td>276.98</td>
<td>167.83</td>
<td>g</td>
</tr>
<tr>
<td>Benzene</td>
<td>82.9</td>
<td>269.2 d</td>
<td>g</td>
</tr>
<tr>
<td>Ethylene Oxide</td>
<td>-52.64</td>
<td>243.00</td>
<td>g</td>
</tr>
<tr>
<td>AcrylonitriLe</td>
<td>179.7</td>
<td>274.1 d</td>
<td>g</td>
</tr>
<tr>
<td>AdiponitriLe</td>
<td>149</td>
<td>400.5 e</td>
<td>g</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>-104.7</td>
<td>270.2 d</td>
<td>g</td>
</tr>
<tr>
<td>Propene</td>
<td>20.41</td>
<td>266.6 d</td>
<td>g</td>
</tr>
</tbody>
</table>

$^a$ Data from NIST unless otherwise specified
$^b$ Data for graphite
$^c$ Data from Dortmund Data Bank
$^d$ Data from Lange’s Handbook of Chemistry
$^e$ Data from RMG using group additivity

S2 Raw reaction thermodynamics for reaction equations
Table S2: Reaction raw thermodynamic parameters. These are the reaction thermochemical parameters used throughout this work (primarily Figure 6). The stoichiometry is normalized as described in Section S7 and the raw data for individual molecules is provided in Table S1.

<table>
<thead>
<tr>
<th>Reaction Stoichiometry</th>
<th>$\Delta H_{\text{rxn}}^0$ (kJ/mol)</th>
<th>$\Delta S_{\text{rxn}}^0$ (J/mol.K)</th>
<th>$\sum_{i \in \text{gas}} \nu_i$</th>
<th>$n_e^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \rightarrow \text{NH}_3$</td>
<td>-45.9</td>
<td>-99.1</td>
<td>-1</td>
<td>3</td>
</tr>
<tr>
<td>$\text{NH}_3 \rightarrow \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2$</td>
<td>45.9</td>
<td>99.1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>CHECK $\text{H}_2 + \text{CO} + \text{C}_2\text{H}_4 \rightarrow \text{Propanal}$</td>
<td>-130.7</td>
<td>-243.3</td>
<td>-2</td>
<td>2</td>
</tr>
<tr>
<td>Propane $\rightarrow \text{Propylene} + \text{H}_2$</td>
<td>125.1</td>
<td>127.1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>$2 \text{H}_2\text{S} + \text{O}_2 \rightarrow 2 \text{S} \ell + 2 \text{H}_2\text{O}$</td>
<td>-439.0</td>
<td>-165.3</td>
<td>-1</td>
<td>4</td>
</tr>
<tr>
<td>6 $\text{CH}_4 \rightarrow \text{Benzene} + 9 \text{H}_2$</td>
<td>530.5</td>
<td>327.8</td>
<td>4</td>
<td>18</td>
</tr>
<tr>
<td>$\text{CO}_2 + 3 \text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$</td>
<td>-53.3</td>
<td>-177.2</td>
<td>-2</td>
<td>6</td>
</tr>
<tr>
<td>$\text{CO} + 2 \text{H}_2 \rightarrow \text{CH}_3\text{OH}$</td>
<td>-94.5</td>
<td>-219.2</td>
<td>-2</td>
<td>4</td>
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<tr>
<td>CHECK 6 $\text{CO}_2 + \text{CH}_4 \rightarrow 2 \text{H}_2 + 2 \text{CO}$</td>
<td>247.0</td>
<td>256.6</td>
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<td>6</td>
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<tr>
<td>$\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$</td>
<td>241.8</td>
<td>44.4</td>
<td>0.5</td>
<td>2</td>
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<tr>
<td>$\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2$</td>
<td>283.0</td>
<td>86.4</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>$\text{N}_2 + 3 \text{H}_2\text{O} \rightarrow 2 \text{NH}_3 + \frac{3}{2} \text{O}_2$</td>
<td>633.7</td>
<td>-64.9</td>
<td>-0.5</td>
<td>6</td>
</tr>
<tr>
<td>2 $\text{CO}_2 + 2 \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_4 + 3 \text{O}_2$</td>
<td>1323.2</td>
<td>29.5</td>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_4 + \text{H}_2\text{O} \rightarrow$</td>
<td>136.7</td>
<td>-34.5</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Ethylene Oxide $+ \text{H}_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 $\text{NaCl} \ (s) + 2 \text{H}_2\text{O} \ell \rightarrow$</td>
<td>542.0</td>
<td>198.6</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$\text{H}_2 + \text{Cl}_2 + 2 \text{NaOH} \ (s)$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 $\text{Al}_2\text{O}_3 \ (s) + 3 \text{C} \ (s) \rightarrow$</td>
<td>2170.9</td>
<td>635.9</td>
<td>3</td>
<td>12</td>
</tr>
<tr>
<td>4 $\text{Al} \ (s) + 3 \text{CO}_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Acrylonitrile $+ \text{H}_2\text{O}$</td>
<td>31.4</td>
<td>-233.9</td>
<td>-1.5</td>
<td>2</td>
</tr>
<tr>
<td>Adiponitrile $+ \frac{1}{2} \text{O}_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Supplemental Experimental Procedures**

**S1 Equilibrium constant**

As in the main text, we will start with a generic chemical equation and a statement of equilibrium at constant $T$, $P$, and $E$:

\[ \sum_i \nu_i A_i = 0 \]  
\[ \sum_i \nu_i \mu_i (T, P, E) = 0 \]

Here, $\nu_i$ is the stoichiometric coefficient for chemical species $A_i$ and $\mu_i$ is the *electrochemical* potential. The influence of applied potential on our system can be expressed as,

\[ \sum_i \nu_i \mu_i (T, P, E) = \sum_i \nu_i \bar{\mu}_i (T, P) + n_e^- FE = 0 \]
where \( n_e^- \) is the minimum number of electrons necessarily transferred in the reaction, \( F \) is Faraday's constant, and \( \bar{\mu}_i(T, P) \) is the chemical potential of species \( i \). Note that in theory, convoluted half-reactions and reaction design can allow for an arbitrary number of electrons to be transferred, but we choose the minimum possible number of electrons given a reaction stoichiometry in order for \( n_e^- \) to have a unique value for each overall reaction stoichiometry (choice of stoichiometry discussed in Supplemental Derivation S7).

We can express the chemical potentials \( (\bar{\mu}_i) \) in terms of the activities \( (a_i) \) and the chemical potentials of the ideal pure substance \( (\bar{\mu}^0_i(T, P^0)) \),

\[
\bar{\mu}_i(T, P) = \bar{\mu}^0_i(T, P^0) + RT \log_a a_i
\]  

(S4)

We can set our reference states such that \( \bar{\mu}_i^0(T, P^0) = \Delta G_f(T, P^0) \) (the Gibbs Free Energies of formation). In addition, we are dealing with an ideal gas mixture—therefore a set of \( n \) components.

Plugging in, we get the following result:

\[
0 = \sum_i \nu_i \mu_i(T, P, E) = n_e^- FE + \sum_i \left[ \nu_i \Delta G_f(T, P^0) + \nu_i RT \log_a \frac{p_i}{P^0} \right]
\]

(S5)

\[
= n_e^- FE + \sum_i \nu_i \Delta G_{rxn}(T, P^0) + RT \log_a \frac{P}{P^0} \sum_i \nu_i \log_a y_i
\]

(S6)

\[
0 = n_e^- FE + \Delta H_{rxn}(T^0, P^0) - T \Delta S_{rxn}(T^0, P^0) + RT \Delta n_{rxn} \log_a \frac{P}{P^0} + RT \log_a K
\]

(S7)

Note we have introduced the variable \( K \equiv \prod_{i \in \text{gas}} y_i^{\nu_i} \). We have implicitly used the assumption that \( \Delta G_{rxn}(T, P^0) = \Delta H_{rxn}(T^0, P^0) - T \Delta S_{rxn}(T^0, P^0) \). In practice, one will use the Gibbs-Helmholtz equation to find \( \Delta G_{rxn}(T, P^0) \) as a function of temperature. If we assume that \( \Delta H_{rxn}(T, P^0) \) and \( \Delta S_{rxn}(T, P^0) \) are not functions of temperature (equivalently that \( \Delta C_{P,rxn} = 0 \)), then the expression used here is accurate. Rearranging the above and taking \( P^0 = 1 \text{ bar} \), we get the result from the main text:

\[
\log_a K = - \frac{\Delta H_{rxn}^0}{RT} - \frac{n_e^- FE}{RT} - \Delta n_{rxn} \log_a \frac{P}{1 \text{ bar}} + \frac{\Delta S_{rxn}^0}{R}
\]

(S8)

Relaxing our assumption \( \Delta C_{P,rxn} = 0 \) so that \( \Delta C_{P,rxn} = \text{const.} \) changes our expression to the following,

\[
\log_a K = \frac{- \Delta H_{rxn}^0}{RT} - \frac{\Delta C_{P,rxn}(T - T^0)}{RT} - \frac{n_e^- FE}{RT} - \Delta n_{rxn} \log_a \frac{P}{1 \text{ bar}} + \frac{\Delta S_{rxn}^0}{R} + \frac{\Delta C_{P,rxn}^0}{R} \log_a \frac{T}{T^0} + \delta_1 - \delta_2
\]

(S9)
We could relax this assumption even further such that \( \Delta C_{P,rxn} = f(T) \), but this would needlessly complicate our equation and has only second order effects on the result for the operating conditions and reactions we are generally considering (Figure S1). In Equation (S10), we have introduced two new terms: \( \delta_1 \) and \( \delta_2 \). \( \delta_2 \propto \log_e \frac{T}{T^0} \), and for \( T < \sim 1500 \text{K} = 5T^0 \) this term will be be approximately \( \frac{\Delta C^0_{P,rxn}}{T} \). \( \delta_1 \) can be analyzed two ways. The first is that it will have two effects: (1) it will add an additional constant term (\( \frac{\Delta C^0_{P,rxn}}{T} \)) to the equilibrium expression and it will change the “effective” enthalpy of reaction by \( \Delta C^0_{P,rxn} T^0 \), likely a small value if \( \Delta C^0_{P,rxn} \) is close to zero. The second way \( \delta_1 \) can be analyzed will be through the lens that \( T^0 < T < \sim 1500 \text{K} = 5T^0 \). Accordingly, \( 0 < \delta_1 < \frac{4}{5} \frac{\Delta C^0_{P,rxn}}{R} \). Because \( \delta_1 \) and \( \delta_2 \) are subtracted and added to Equation (S10), respectively, we see that together they actually result in a negligible contribution to our expression that qualitatively changes nothing about our results as long as \( \Delta C^0_{P,rxn} \ll \Delta H^0_{rxn} \).

Figure S1: Comparison of equilibrium constant for ammonia synthesis reaction (Equation R1) given the assumptions in the main text (A) and for “real” thermodynamic data taken from NIST (B). They are qualitatively the same, and quantitatively the real equilibrium constant is less than 0.8 logarithmic units lower than it is with our assumptions even at 1500 K.

We have assumed that all of our species are gas phase. If we have species that are liquids or solids, we can replace the activities \( a_i = 1 \), which results in \( \Delta n_{rxn} = \sum_{i \in \text{gas}} n_i \) and \( K \) is only a function of the mole fractions in the gas phase.

To adjust for solvated species reactions, we would change the activity to be a concentration \( (c_i) \) instead of a partial pressure and our equilibrium constant would be a function of the system volume. This is beyond the scope of this work but remains a useful exercise for understanding solvated systems which are ubiquitous to electrochemistry.
S2 Relationship between equilibrium constant $K$ and conversion

As mentioned in the main text, we generally are looking for a value for the thermodynamic conversion, $z \in [0, 1]$, when analyzing a reaction since conversion is a much more meaningful quantity to work with when designing reactors than an equilibrium constant. Unfortunately, each reaction will have a slightly different expression for conversion as a function of the equilibrium constant, $z = z(K)$, depending on the stoichiometry. However, there are some commonalities in all of these conversion functions that mean that using $K$ as a proxy for conversion is reasonable. We have shown a couple functions for conversion in terms of the equilibrium constant (Figure S2), where the strict increasing nature of the conversion function is evident. Conversion will in general always be a sigmoidal, increasing function of $K$, similar to the logistic function ($\text{logit}(x) = \frac{1}{1+e^{-x}}$). Moreover, $z$ will generally span the full range from 0 to 1 in the domain $-5 < \log_{10} K < 5$ regardless of stoichiometry. Because we are normalizing our stoichiometries (Discussion S7), our conversion functions are even more likely to have a similar shape and range.

![Figure S2](image.png)

Figure S2: One of the main assumptions the analysis relies upon is that the equilibrium constant ($K$) is a proxy for conversion. Here, the conversion as a function of the equilibrium constant is shown for multiple different reaction stoichiometries assuming initial stoichiometric quantities of reactants and zero products (solid lines) as well as for the logistic function, logit. As can be seen, conversion is strictly increasing and generally has a similar sigmoidal shape as a function of $K$ for any reaction stoichiometry. Therefore, $K$ is a reasonable proxy for conversion.

In order to derive an exact expression for $z$ as a function of $K$ given a reaction stoichiometry, we will use the common RICE method (Reaction, Initialization, Change, Equilibrium). For example,

We can then write an expression for $K = \prod_i y_i$ and solve for conversion, $z = \epsilon$, as a function of $K$ algebraically or numerically.
Table S3: RICE method for $A + B \rightarrow C + D$

<table>
<thead>
<tr>
<th>R</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>$-\epsilon$</td>
<td>$-\epsilon$</td>
<td>$\epsilon$</td>
<td>$\epsilon$</td>
</tr>
<tr>
<td>E</td>
<td>$1 - \epsilon$</td>
<td>$1 - \epsilon$</td>
<td>$\epsilon$</td>
<td>$\epsilon$</td>
</tr>
</tbody>
</table>

S3 Non-dimensionalization of equilibrium expression

In general, there are multiple ways to non-dimensionalize Equation (S9). When working with partial differential equations, such as the Navier-Stokes equation, non-dimensionalization involves rescaling every quantity by some physical characteristic property so that the variables are order 1 and dimensionless groups such as the Reynolds number are prefactors to parts of the equation. These dimensionless groups make experimental probing of a system simpler since the number of parameters affecting the system has been reduced, and they also make the practical aspects of solving the equations easier either analytically or numerically. In our case, however, we do not have a differential equation, and we want to find an expression for $\log_{10} K$ that is independent of the exact chemical reaction.

Our system is not so amenable to pulling out a simple non-dimensional grouping, so we instead focus on finding characteristic physical parameters that can remove any reaction-specific information from our expression. Our first parameter is temperature. There are multiple options for a characteristic temperature, which we will briefly discuss. The first is $T_{\text{char}} = \Delta H_{\text{rxn}}^0 / \Delta S_{\text{rxn}}^0$. This characteristic temperature is essentially the temperature at which $K = 1$ and pops out from $0 = \Delta G_{\text{rxn}}^0 = \Delta H_{\text{rxn}}^0 - T_{\text{char}} \Delta S_{\text{rxn}}^0$. However, this temperature is not ideal because it can be negative, and for reactions that are thermodynamically favored at ambient conditions, this value provides a poor scaling for the operating temperature. If we instead look directly at Equation (S9), we see that the first term has a natural characteristic temperature already in it: $T_{\text{char}} \equiv \Delta H_{\text{rxn}}^0 / R$. This additionally provides us with a natural energy scaling, $\Delta H_{\text{rxn}}^0$. Of course, this brings up the question, why not use $\Delta G_{\text{rxn}}^0$ as an energy scaling since it is perhaps a more relevant quantity for reaction conversion? Unfortunately, using the Gibbs free energy as our characteristic energy results in a needlessly complicated expression for $K$ that makes the entire analysis less intuitive. One last detail is that we chose to define our non-dimensional temperature quantity as $\alpha T$ instead of $1/T$ because the scaling is more intuitive with the direct proportionality.

Given a characteristic energy scaling, a characteristic voltage is simply, $E_{\text{char}} \equiv \frac{\Delta H_{\text{rxn}}^0}{n_e F}$. The last parameter we need to take care of is pressure. Pressure is different from the rest because it already has a characteristic pressure (the reference pressure, 1 bar) built into the equilibrium expression. However, we still want to remove any dependence on $\Delta n_{\text{rxn}}$. If we did not want to include the logarithm in our non-dimensional quantity, we would end up with $\Pi = \left( \frac{p}{p_0} \right)^{\Delta n_{\text{rxn}}}$. This, however, is even less intuitive of a non-dimensional pressure than simply wrapping up the entire term into a non-dimensional quantity. As a result, including a change of base so that our expression is in base 10 instead of base $e$, we get the following.
expressions from the main text:

$$\Theta \equiv \frac{RT \log_{10} 10}{\Delta H_{\text{rxn}}}, \quad (S11)$$

$$\Pi \equiv \Delta n_{\text{rxn}} \log_{10} \frac{P}{P_0}, \quad (S12)$$

$$\Psi \equiv \frac{n_e F E}{\Delta H_{\text{rxn}}^0}, \quad (S13)$$

$$\sigma \equiv \frac{\Delta S_{\text{rxn}}}{R \log_{e} 10}, \quad (S14)$$

$$\log_{10} K = -\frac{1}{\Theta} \left( -\frac{\Psi}{\Theta} - \Pi + \sigma \right). \quad (S15)$$

While this justification for non-dimensional groupings may appear slightly arbitrary, it not only results in a simple equilibrium expression but also has a physical basis in the work and heat exchanges with our system, as discussed in the main text.

**S4  Constant $K$ contours and comparison of driving forces**

Our non-dimensional equation is:

$$\log_{10} K = -\frac{1}{\Theta} \left( -\frac{\Psi}{\Theta} - \Pi + \sigma \right) \quad (S16)$$

We can see that the level curves for a given $K$ at no applied potential ($\Psi = 0$) result in an inverse relationship between $\Pi$ (base 10 logarithm of pressure) and $\Theta$ (temperature):

$$\Pi = (\sigma - \log_{10} K) - \frac{1}{\Theta} \quad (S17)$$

Similarly, we can see that the level curves for a given $K$ at ambient pressure ($\Pi = 0$) result in a linear relationship between $\Psi$ (potential) and $\Theta$ (temperature):

$$\Psi = \Theta (\sigma - \log_{10} K) - 1 \quad (S18)$$

Last, we can see that the level curves for a given $K$ at ambient temperature ($\Theta = \Theta_{\text{ambient}}$) result in a linear relationship between $\Psi$ (potential) and $\Pi$ (pressure):

$$\Pi = -\frac{1}{\Theta_{\text{ambient}}} (1 + \Psi) - \log_{10} K + \sigma \quad (S19)$$

These are the equations used to draw constant $K$ contours in the main text (reproduced in Figure S4). Note that the constant $K$ contours for a pressure-voltage relationship are not reaction-independent due to the appearance of $\Theta_{\text{ambient}}$, such that this cannot be plotted in universal form, as we are able to do in the two other cases (Figure S3). Because a voltage-pressure plot is not generalizable to all chemical reactions, we do not discuss it in detail and assume that our system relies on either voltage as a driving force ($\Pi = 0$) or pressure as a driving force ($\Psi = 0$), but not both simultaneously.
Figure S3: Pressure-voltage contour plot with $\Theta_{\text{ambient}} = 0.1$. Unlike the pressure-temperature and voltage-temperature plots, a pressure-voltage plot depends $\Theta_{\text{ambient}}$ which means it depends on $\Delta H_{\text{rxn}}$ (Equation S15). For this reason, it is not a universal colormap and we have included it here for completeness of visualization only. $\Theta_{\text{ambient}} = 0.1$ was chosen arbitrarily, but different values of the enthalpy of reaction will change the magnitude and sign of the contours’ slopes.

As seen visually in Figure S4, both temperature ($\Theta$) and potential ($\Psi$) can easily cross contours of constant $\log_{10} K$, making them powerful thermodynamic tools. Pressure, however, cannot cross constant $K$ contours as easily, requiring a large change in pressure to alter the conversion (keep in mind that $\Pi \propto \log_{10} P$ so an order of magnitude change in $P$ is necessary to change $\Pi$). Simply by looking at the colormaps of Equation S15, one can see that qualitatively potential is a better choice than pressure for improving conversion.

We can better compare these thermodynamic driving forces quantitatively by comparing the derivatives of $\log_{10} K$ with respect to each variable. Taking the partial derivatives of Equation S15 we get:

$$(\frac{\partial \log_{10} K}{\partial \Pi})_{\Theta, \Psi} = -1 \quad (S20)$$

$$(\frac{\partial \log_{10} K}{\partial \Theta})_{\Pi, \Psi} = \frac{1}{\Theta^2} (1 + \Psi) \quad (S21)$$

$$(\frac{\partial \log_{10} K}{\partial \Psi})_{\Theta, \Pi} = -\frac{1}{\Theta} \quad (S22)$$

We can see right away from these derivatives that, given $\Theta < 1$ (generally true for reasonable reaction enthalpies and operating temperatures, Table S4), $\log_{10} K$ will scale more favorably with voltage ($\Psi$) and temperature ($\Theta$) than with pressure ($\Pi$). Additionally, given that $\Pi \propto \log_{10} P$, $K$ has a logarithmic relationship with pressure, making it a relatively poorer driving force compared to temperature and voltage. In order to better compare
Figure S4: Plots of Equation S15 reproduced from main text. Every reaction can be mapped onto these plots. When no voltage is applied (Ψ = 0), the contours of how pressure and temperature affect the equilibrium are visualized (left). At ambient pressure (Π = 0), the contours of how voltage and temperature affect the equilibrium are visualized (right). Qualitatively, crossing the constant $K$ contours using pressure is more difficult than using voltage or temperature. Note that the colorbar axis is $\log_{10} K - \sigma$ so that the plot remains independent of reaction; different reactions will essentially provide a constant shift from $\sigma$ that does not change the shape of the plot. Note that crossing $\Theta = 0$ for a given reaction is impossible since the sign of $\Theta$ is determined by the reaction enthalpy (a fixed quantity assuming $\Delta C_{P,rxn} = 0$).

These derivatives further support that qualitatively, crossing voltage and temperature contours is easier and more effective than crossing pressure contours since they have relatively larger derivatives than the derivative with respect to $\Pi$. We additionally see that at low values of $\Psi$, crossing voltage contours may be less effective, but that with moderate to large
values of $\Psi$ ($\Psi$ can easily increase above 2 in some reactions with smaller $|\Delta H_{\text{rxn}}^0|$, Table S4), crossing voltage contours becomes significantly more effective than crossing pressure contours. Crossing temperature contours remains perhaps the most effective at increasing $K$, but temperature is limited in that we cannot practically go to operating temperatures above ca. 1500 K, which is insufficient to drive some reactions.

We have so far stated as fact that $\Theta < 1$ for many reactions, and to back this up, I have provided values for $\Theta_{\text{ambient}}$ for ammonia synthesis and water splitting:

$$\frac{1}{2} N_2 + \frac{3}{2} H_2 \rightarrow NH_3, \quad \text{(R1)}$$

$$H_2O \rightarrow H_2 + \frac{1}{2} O_2. \quad \text{(R2)}$$

Table S4: Reaction parameters for ammonia synthesis and water splitting

<table>
<thead>
<tr>
<th>Rxn</th>
<th>$\Delta H_{\text{rxn}}^0$ (kJ/mol)</th>
<th>$\Delta S_{\text{rxn}}^0$ (J/mol.K)</th>
<th>$\sum_{i=\text{gas}} \nu_i$</th>
<th>n</th>
<th>$\Theta_{\text{ambient}}$</th>
<th>$E_{\text{at}} \Psi = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eq. R1</td>
<td>-46</td>
<td>-99</td>
<td>-1</td>
<td>3</td>
<td>-0.12</td>
<td>-0.16 V</td>
</tr>
<tr>
<td>Eq. R2</td>
<td>242</td>
<td>44</td>
<td>0.5</td>
<td>2</td>
<td>0.024</td>
<td>1.25 V</td>
</tr>
</tbody>
</table>

We can see that for these very different reactions, $\Theta_{\text{ambient}}$ and $\Psi$ have values as we have described above.

S5 Derivation of work and energy exchange

We want to convert our chemical reaction system away from the variables $T$, $P$, and $E$, which are not directly comparable, to quantities that are directly comparable. In particular, we want to compare relevant work and energy quantities for our system, specifically mechanical work input ($\dot{W}_{M,\text{on}}$), heat input ($\dot{Q}_{\text{on}}$) and electrochemical work input ($\dot{W}_{E,\text{on}}$). All of these parameters have units of Watts, and we will assume continuous, steady state operation of our system with each step being reversible. Additionally, we will continue to assume that all of our mixtures are ideal mixtures of ideal gases. As we all know from thermodynamics, work and heat flow are path variables and should depend on exactly how we operate our system. However, if we constrain our system to operate with one heat bath (e.g., the atmosphere), then all reversible paths will result in the same work and heat flux. We have introduced one additional parameter to our system, $T^{\text{bath}}$, but in return work and heat flux become state functions.

The system we will work with is shown in Figure S5, a variation on a Van’t Hoff Equilibrium box. In particular, we will first change our system from ambient conditions to reaction conditions, operate the reaction for some extent of reaction at constant $T$, $P$, and $E$, and then return our system to ambient conditions.

We will treat each sub-unit of Figure S5 in turn. First, let’s look at the unit that changes the $T$ and $P$ to operating conditions. We can do an entropy (Second law) balance over this
Figure S5: Model for calculating work and heat flow for our system. Each box is a separate unit we will analyze as described in the text. Note that as written, \( \dot{n}_{\text{in}} \) and \( \dot{n}_{\text{out}} \) are vectors of mole flowrates with \( \dot{n}_{\text{out}} = \dot{n}_{\text{in}} - \xi \nu \) (\( \xi \) is the extent of reaction between 0 and 1 and \( \nu \) is a vector of the stoichiometric coefficients)

We have assumed steady state (\( \dot{S}_{\text{unit}} = 0 \)) and reversible (\( \dot{S}_{\text{universe}} = 0 \)), and have used the entropy for an ideal gas. Additionally, \( R \) is the ideal gas constant and \( C_{P,\text{rxts}} \) is the molar average \( C_P \) of the reactant mixture. We can next perform an energy (First Law) balance to get the mechanical work on the system.

\[
\dot{U} = \dot{Q}_{\text{on}} + \dot{W}_{M,\text{on}} + \dot{n}_{\text{in}} H(T_0, P_0, E_0) - \dot{n}_{\text{in}} H(T, P, E)
\]

(31)

\[
\dot{W}_{M,\text{on}} = \dot{n}_{\text{in}} C_{P,\text{rxts}} (T - T_0) - \dot{n}_{\text{in}} T_{\text{bath}} (C_{P,\text{rxts}} \log \frac{T}{T_0} - R \log \frac{P}{P_0})
\]

Again, we have assumed steady state and an ideal gas with the enthalpy being only a function of temperature. A few important items to note about these equations: First, we need to specify \( T_{\text{bath}} \). We chose this additional parameter instead of a specific thermodynamic path to increase generality of our analysis. In practice, though, our derivation is not so different from an adiabatic compressor followed by a heat exchanger. Second, because our path is reversible, the work and heat flow on the unit after the reactor will essentially be the same expression except with \( \dot{n}_{\text{out}} \) instead of \( \dot{n}_{\text{in}} \) and \( C_{P,\text{rds}} \) instead of \( C_{P,\text{rxts}} \). Third, because our system is reversible, the work we calculate is the maximum possible work by our system (or the minimum work on our system).

The remaining unit we need to analyze is the reaction unit itself (the post-reactor unit is identical to the pre-reactor unit with some sign changes). We will follow the same procedure as above. Since our reaction is at constant T and P, the environment must also be at T and P for the sake of thermodynamic consistency in our derivation. First, a second law balance gives:
\[ \dot{Q}_{\text{on}} = \dot{\xi} T \left( \Delta S_{\text{rxn}}^0 + \Delta C_{P,\text{rxn}} \log \frac{T}{T_0} - \Delta n_{\text{rxn}} R \log \frac{P}{P_0} \right) \quad (S32) \]

\[ = \dot{\xi} T \Delta S_{\text{rxn}} \quad (S33) \]

A first law energy balance gives:

\[ \dot{W}_{M,\text{on}} + \dot{W}_{E,\text{on}} = -\dot{\xi} T \left( \Delta S_{\text{rxn}}^0 + \Delta C_{P,\text{rxn}} \log \frac{T}{T_0} - \Delta n_{\text{rxn}} R \log \frac{P}{P_0} \right) + \dot{\xi} \left( \Delta H_{\text{rxn}}^0 + \Delta C_{P,\text{rxn}} (T - T^0) \right) \quad (S34) \]

\[ = \dot{\xi} \Delta G_{\text{rxn}}(T, P) \quad (S35) \]

This makes intuitive sense, but does not allow for the case where the reaction does not allow for mechanical work and the reaction’s mechanical work is dissipated as heat. Incorporating the known electrical work allows us to write the following expressions:

\[ \dot{W}_{E,\text{on}} = -\dot{\xi} nFE \quad (S36) \]

\[ \dot{W}_{M,\text{on}} \leq \dot{\xi} \left( \Delta G_{\text{rxn}}(T, P) + nFE \right) \quad (S37) \]

\[ \dot{Q}_{\text{on}} = \dot{\xi} \left( \Delta H_{\text{rxn}}^0 + \Delta C_{P,\text{rxn}} (T - T^0) \right) - \left( \dot{W}_{M,\text{on}} + \dot{W}_{E,\text{on}} \right) \quad (S38) \]

Combining Equations S36, S37, and S38 along with Equations S28 and S31 for the pre and post change in state give us an expression for the total work and heat flow of the entire system.

\[ \dot{W}_{E,\text{on}} = \eta_{\text{rxn},W} \dot{W}_{E,\text{rxn}} \quad (S39) \]

\[ \dot{W}_{M,\text{on}} = \eta_{\text{pre},W} \dot{W}_{M,\text{pre}} + \eta_{\text{rxn},W} \dot{W}_{M,\text{rxn}} + \eta_{\text{post},W} \dot{W}_{M,\text{post}} \quad (S40) \]

\[ \dot{Q}_{\text{on}} = \eta_{\text{pre},Q} \dot{Q}_{\text{pre}} + \eta_{\text{rxn},Q} \dot{Q}_{\text{rxn}} + \eta_{\text{post},Q} \dot{Q}_{\text{post}} \quad (S41) \]

Here all of the \( \eta_i \) represent efficiencies that can be put in if more information is know about a system (e.g., if you will not be using an expander to retrieve work \( \eta_{\text{post},W} = 0 \)). For the sake of analysis, we will assume that all \( \eta_i = 1 \), representing the theoretical minimum work performed on our system and its corresponding heat flow. We then get the following expression for the total work and heat flow in our system given a certain \( T \) and \( P \) (remember that the extent of reaction is also just a function of \( T \) and \( P \)). In this derivation we assume that mechanical work can be exchanged with the reactor.
\[
\dot{W}_{\text{M,on}} = (\dot{n}_{\text{in}} C_{P,\text{rxn}} - \dot{n}_{\text{out}} C_{P,\text{prds}})(T - T_0)
- T^{\text{bath}} \left( (\dot{n}_{\text{in}} C_{P,\text{rxn}} - \dot{n}_{\text{out}} C_{P,\text{prds}}) \log \frac{T}{T_0} - (\dot{n}_{\text{in}} - \dot{n}_{\text{out}}) R \log \frac{P}{P_0} \right)
+ \dot{\xi} (\Delta G_{\text{rxn}}(T, P) + nFE)
= -\dot{\xi} \Delta C_{P,\text{rxn}}(T - T_0) + \dot{\xi} T^{\text{bath}} \left( \Delta C_{P,\text{rxn}} \log \frac{T}{T_0} - \Delta n_{\text{rxn}} R \log \frac{P}{P_0} \right)
+ \dot{\xi} (\Delta G_{\text{rxn}}(T, P) + nFE)
\]

\[
\dot{W}_{\text{M,on}} = \dot{\xi} \left( \Delta C^0_{\text{rxn}} + (T^{\text{bath}} - T) \left[ \Delta C_{P,\text{rxn}} \log \frac{T}{T_0} - \Delta n_{\text{rxn}} R \log \frac{P}{P_0} \right] + nFE \right)
\]

\[
\dot{Q}_{\text{on}} = T^{\text{bath}} \left( (\dot{n}_{\text{in}} C_{P,\text{rxn}} - \dot{n}_{\text{out}} C_{P,\text{prds}}) \log \frac{T}{T_0} - (\dot{n}_{\text{in}} - \dot{n}_{\text{out}}) R \log \frac{P}{P_0} \right)
+ \dot{\xi} (\Delta H^0_{\text{rxn}} + \Delta C_{P,\text{rxn}}(T - T^0) - \Delta G_{\text{rxn}}(T, P))
= -\dot{\xi} T^{\text{bath}} \left( \Delta C_{P,\text{rxn}} \log \frac{T}{T_0} - \Delta n_{\text{rxn}} R \log \frac{P}{P_0} \right)
+ \dot{\xi} \left( \Delta H^0_{\text{rxn}} + \Delta C_{P,\text{rxn}}(T - T^0) - \Delta G_{\text{rxn}}(T, P) \right)
\]

\[
\dot{Q}_{\text{on}} = \dot{\xi} \left( T \Delta S^0_{\text{rxn}} - (T^{\text{bath}} - T) \left[ \Delta C_{P,\text{rxn}} \log \frac{T}{T_0} - \Delta n_{\text{rxn}} R \log \frac{P}{P_0} \right] \right)
\]

\[
\dot{W}_{\text{E,on}} = -\dot{\xi} nFE
\]

If we assume that no mechanical work can be exchanged with the reactor (a reasonable industrial situation that corresponds to us relaxing the constraint \( \dot{S}_{\text{universe}} = 0 \) for the reactor unit itself), we get the following:

\[
\dot{W}_{\text{E,on}} = -\dot{\xi} nFE
\]

\[
\dot{W}_{\text{M,on}} = \dot{\xi} \left( -\Delta C_{P,\text{rxn}}(T - T_0) + T^{\text{bath}} \left[ \Delta C_{P,\text{rxn}} \log \frac{T}{T_0} - \Delta n_{\text{rxn}} R \log \frac{P}{P_0} \right] \right)
\]

\[
\dot{Q}_{\text{on}} = \dot{\xi} \left( -T^{\text{bath}} \left[ \Delta C_{P,\text{rxn}} \log \frac{T}{T_0} - \Delta n_{\text{rxn}} R \log \frac{P}{P_0} \right] + \Delta H^0_{\text{rxn}} + \Delta C_{P,\text{rxn}}(T - T_0) + nFE \right)
\]

Interestingly enough, even though we began this analysis allowing enthalpy to vary with temperature, we find that in these final expressions for work and heat flow that the enthalpic terms all contain \( \Delta C_{P,\text{rxn}} \). We previously assumed this value to be zero, and while this is not a good assumption for quantitative results, it is a reasonable assumption to qualitatively study the system. From here forward, we will assume that no mechanical work is exchanged between the reactor and the environment. With these assumptions, we get the following expressions for work and heat flows:
\[ \dot{W}_{E,\text{on}} = -\dot{\xi} n FE \] (S57)

\[ \dot{W}_{M,\text{on}} = -\dot{\xi} \Delta n_{\text{rxn}} RT_{\text{bath}} \log \frac{P}{P_0} \] (S58)

\[ \dot{Q}_{\text{on}} = \dot{\xi} \left( \Delta n_{\text{rxn}} RT_{\text{bath}} \log \frac{P}{P_0} + \Delta H^0_{\text{rxn}} + n FE \right) \] (S59)

These are remarkably simple expressions that still make qualitative sense. The electrical work depends on the voltage and conversion by definition. The mechanical work depends on the conversion and the pressure, with any temperature terms having been neglected at this point in the simplification. The heat flow is a function of the reaction enthalpy, the pressure, and the potential as well as conversion. We note that temperature does not appear explicitly in these expressions due to the fact that the temperature components cancel out to enough of a degree that we neglect them with our assumption that the enthalpy of reaction is independent of temperature. However, these expressions still depend strongly on temperature since the conversion will depend strongly on temperature.

A major assumption that we are making is that the heat bath used to bring the reactants to operating conditions and the heat bath used to bring the products to ambient conditions is at the same \( T_{\text{bath}} \). This is likely a poor assumption in practice, but for the sake of qualitative analysis it is sufficient to give us an idea of the functional form of the work and heat flux terms in terms of simple parameters while avoiding complications from the various heat capacities of reactants and products.

As it turns out, we can write our equations for work and heat flow in non-dimensional form as in the main text. Let us define new non-dimensional quantities:

\[ \Omega_{W,E} = \frac{\dot{W}_{E,\text{on}}}{\Delta H^0_{\text{rxn}}} \] (S60)

\[ \Omega_{W,M} = \frac{\dot{W}_{M,\text{on}}}{\Delta H^0_{\text{rxn}}} \] (S61)

\[ \Omega_Q = \frac{\dot{Q}_{\text{on}}}{\Delta H^0_{\text{rxn}}} \] (S62)

Additionally, note that \( \dot{\xi} = z(\log_{10} K_{eq}) = z(f(\Theta, \Psi, \Pi) + \sigma) \), where \( f = -1/\Theta - \Psi/\Theta - \Pi \). The exact function form of \( \dot{\xi} \) depends on the reaction, but we know it is roughly logistic in shape and spans 0 to 1 from \( \log_{10} K_{eq} = -5 \) to \( \log_{10} K_{eq} = 5 \), respectively.

We can now write:

\[ \Omega_{W,E} = -z(f(\Theta, \Psi, \Pi) + \sigma) \Psi \] (S63)

\[ \Omega_{W,M} = -z(f(\Theta, \Psi, \Pi) + \sigma) \Theta_{\text{bath}} \Pi \] (S64)

\[ \Omega_Q = z(f(\Theta, \Psi, \Pi) + \sigma)(\Theta_{\text{bath}} \Pi + \Psi + 1) \] (S65)

Our equations for work and heat are easily nondimensionalized with our nondimensional groups from the discussion on chemical equilibrium. Note that as expected, energy for the
entire process is conserved:

\[
\sum_i \Omega_i = z(f(\Theta, \Psi, \Pi) + \sigma)
\]

(S66)

What we get from Equation S66 is intuitive: all of the energy exchange with our system must add up to the conversion times the enthalpy of reaction (this is just conservation of energy). Note that this equivalence of energy

S6 Redefinition of axes to collapse \(K\) contours

We would like to compare many reactions to each other on the same set of axes. This requires a set of axes on which the equilibrium contours are the same for every reaction. Specifically, we need our contours \((z\text{-levels})\) to be \(\log_{10} K\) instead of \(\log_{10} K - \sigma\). If we look back at Equation (S15), we see that incorporating \(\sigma\) into our \(x\)-axis or \(y\)-axis is nontrivial. In fact, there are a few different ways we could redefine the axes.

Perhaps the simplest redefinition would be to keep the axes as close as possible to the original non-dimensional variables. Accordingly, we can set \(x = \Theta\) and \(y = \Pi - \sigma\) for the pressure-temperature case, meaning that \(\log_{10} K = -1/x - y\). Similarly, for the voltage-temperature case, we would have \(x = \Theta\) and \(y = \Psi - \sigma\Theta\), meaning that \(\log_{10} K = -1/x - y/\Theta\). This formulation could work, but we are stuck with two plots with different equations for equilibrium contours, making interpretation difficult. If we wanted to combine the influence of voltage and pressure onto one axis so that we can describe reactions on a single plot, we could define \(x = \Theta\) and \(y = \Psi/\Theta + \Pi - \sigma\), meaning that \(\log_{10} K = -1/x - y/\Theta\). While this method results in a single plot for comparing pressure, voltage, and temperature, it does not facilitate easy comparison of reactions. Intuitively, reactions with larger enthalpies \((\Delta H_{\text{rxn}}^0)\) will have smaller values of \(\Theta_{\text{ambient}}\) since \(\Theta \propto 1/\Delta H_{\text{rxn}}^0\), but comparing reactions quantitatively by inspection is difficult. Instead, it would be extremely useful if we could represent a reaction by a single point, \((x, y)_{\text{ambient, rxn}}\), such that the point itself was informative about the reaction relative to equilibrium contours and such that we would “add” reaction points \((x_1, y_1)_{\text{ambient, rxn, 1}}\) and \((x_2, y_2)_{\text{ambient, rxn, 2}}\) to generate a new reaction point \((x_1 + x_2, y_1 + y_2)_{\text{ambient, rxn}}\) that represents adding the two reaction chemical equations as well (this is discussed further in the main text). Accordingly, we need to define \(x = 1/\Theta\) and \(y = \Psi/\Theta + \Pi - \sigma\), meaning \(\log_{10} K = -x - y\). This means that constant contours on this axis will be of the form \(y = -x - \log_{10} K\). As an additional benefit, these parallel lines are easier to visualize and compare to reaction points than the contours would be if we had defined \(x = \Theta\) (those contours being represented by \(y = -1/x - \log_{10} K\)).

There are a few points to note on these new axes. As noted in the main text, each reaction is given by the point:

\[
(x, y)_{\text{ambient, rxn}} = \left(\frac{1}{\Theta_{\text{ambient}}}, -\sigma\right) = \left(\frac{\Delta H_{\text{rxn}}^0}{RT^0 \log 10}, -\frac{\Delta S_{\text{rxn}}^0}{RT^0 \log 10}\right)
\]

(S67)

The equilibrium potential for a given reaction is defined by the potential when \(\log_{10} K = 0\), or when \(y = -x\) in these coordinates. At ambient conditions, we know that \(\Psi_{\text{eq}}/\Theta_{\text{ambient}} - \sigma\)
σ = yeq = −xambient. From this, we can get:

\[ \Psi_{eq} = \Theta_{ambient}(yeq + \sigma) \]  
\[ = \Theta_{ambient}(yeq - y_{ambient}) \]  
\[ = \frac{(yeq - y_{ambient})}{x_{ambient}} \]  
\[ = -\frac{(yeq - y_{ambient})}{yeq} \]  
\[ = -1 + \frac{y_{ambient}}{yeq} \]  
\[ \Psi_{eq} = -1 - \frac{y_{ambient}}{y_{eq}} \]  
\[ \Psi_{eq} = -1 - \frac{y_{ambient}}{x_{ambient}} \]  

We can see that the *non-dimensional* equilibrium potential is proportional to the ratio of \( y_{ambient} \) to \( y_{eq} \), or equivalently the ratio \( y_{ambient} \) to \( x_{ambient} \) which is the slope of a line from \((0, 0)\) to \((x, y)_{ambient} \), a simple and intuitive read from the plot. However, there is an even simpler measure of equilibrium potential available from this plot that makes these axes extremely powerful and is described in detail in Discussion [S7](#).

In these redefined axes, a change in voltage or pressure will result in a vertical movement on the axes, and an increase (decrease) in temperature corresponds to a movement toward (away from) the point \((0, \Pi - \sigma)\) (movement along the line given by \( y = -\sigma + \Pi + \Psi x \)). A reproduction of the comparison of multiple reactions from the text if provided with the addition of vertical lines representing an increase in pressure by an order of magnitude (Figure [S6](#)).

### S7 Scaling of reaction stoichiometry to compare reactions

In order to make a proper comparison between reactions, we need to normalize the stoichiometry. To do this, each reaction is scaled to a fixed number of electrons transferred in the reaction (fixed \( n_{e^-} \)). This means that each of \( \Delta H_{rxn}, \Delta S_{rxn}, \) and \( \Delta n_{rxn} \) are rescaled such that \( n_{e^-} = \rho \). The big question is: what value of \( \rho \) should be used? A value between 1 and 4 makes the most sense as it leads to reactions collapsing visually on these axes such that the reactions can be compared easily while still being spaced sufficiently apart. To aid with readability, it makes sense to scale to a number that will result in a meaningful point \((x, y)\). We have therefore chosen to scale to \( n_{e^-} = 2.956 \). This value, although it appears arbitrary, is actually chosen such that a reaction at point \((x, y)\) will have a *dimensional* equilibrium potential \( E_{eq} = -20(x + y) \) (\( E_{eq} \) in mV).

We can see that for a reaction defined by,

\[ (x, y)_{ambient} = \left( \frac{1}{\Theta RT}, -\sigma \right) = \left( \frac{\Delta H^0_{rxn}}{RT^0 \log 10}, -\frac{\Delta S^0_{rxn}}{R \log 10} \right) \]  

the sum of the coordinates is
Figure S6: Reproduction from main text of comparison of multiple reactions on the same axes. Each point represents a chemical reaction, with color denoting whether the reaction is typically conducted thermochemically (pink) or electrochemically (blue). Each reaction point is such that $(x, y)_{\text{ambient}} \propto (\Delta H^0_{\text{rxn}}, -\Delta S^0_{\text{rxn}})$ and can be interpreted as described in Figure S7. Vertical lines represent an increase in pressure by one order of magnitude. The green shading indicates the area where an elevated temperature of less than $\sim 1500$ K can reach $K = 1$, and a quantitative visual divide based on reaction enthalpies and entropies distinguishes between reactions driven with electrochemistry versus those driven with thermochemistry. Note that the stoichiometry depicted in the legend is for readability; all reactions have been scaled to have the same number of electrons for best comparison (Supplemental Derivation S7). To be consistent, chemical formulas were used for all species in the legend, but the following formulas are not unique and refer to the specified chemical: $\text{C}_3\text{H}_6\text{O}$ (propanal), $\text{C}_2\text{H}_4\text{O}$ (ethylene oxide), $\text{C}_3\text{H}_6$ (propene), $\text{C}_6\text{H}_6$ (benzene), $\text{C}_3\text{H}_3\text{N}$ (acrylonitrile), and $\text{C}_6\text{H}_8\text{N}_2$ (adiponitrile). Raw thermodynamic data given in Tables S1 and S2.

\begin{align}
(x + y) &= \frac{\Delta H^0_{\text{rxn}}}{RT^0 \log 10} - \frac{\Delta S^0_{\text{rxn}}}{R \log 10} \tag{S75} \\
&= \frac{\Delta G^0_{\text{rxn}}}{RT^0 \log 10} \tag{S76} \\
&= -\frac{n_e^- F}{RT^0 \log 10} E^\text{eq} \tag{S77}
\end{align}

Solving for $n_e^-$ such that $\frac{F}{RT^0 \log 10} = -0.05$ mV$^{-1}$ (arbitrarily chosen so that the points will be well spaced on the plot and the numbers will be easy for mental math) gives $n_e^- = 2.956$. Unlike previously where we equated the non-dimensional equilibrium potential with a ratio of $y_{\text{ambient}}^\text{ambient}$ to $x_{\text{ambient}}^\text{ambient}$, here we see that the dimensional equilibrium potential can be read directly from this plot. As a corollary to this fact, we can see that reaction points that have $|E^\text{eq}| \leq 1$ V must satisfy the condition that $1000$ mV $\geq | -20(x + y)|$, or equivalently must satisfy $-50 - x \leq y \leq 50 - x$. Although we have not drawn these lines, they unsurprisingly show that voltages of order 1 V are sufficient to drive thermodynamic conversion of most chemical reactions encountered in the wild.
Figure S7: Reproduction from main text. Redefined axes such that all reactions have the same equilibrium $K$ contours. A contour corresponding to $K = 1$ is indicated with a diagonal black line. The filled red diamonds represent an example reaction point at ambient conditions given by Equation (S67). An increase in either pressure ($\Pi$) or voltage ($\Psi$) is a vertical movement on these axes (A, new reaction point given by blue square) and an increase in temperature ($\Theta$) is a movement towards the point $(0, \Pi - \sigma)$ (A, new reaction point given by blue circle, movement along the line connecting to the empty blue diamond). As shown, the distance from the reaction point to the $y$-axis is proportional to $\Delta H^0_{\text{rxn}}$, the distance to the $x$-axis is proportional to $\Delta S^0_{\text{rxn}}$, and the distance to the solid black line ($y = -x$) is proportional to the dimensional equilibrium potential of the reaction (B). Further details in Supplemental Derivations S5 and S6

S8 Quantitative limits on thermochemical and electrochemical reactions

In the main text, we have chosen $\sim 1500 \text{ K}$ as an upper limit for practical temperatures for thermochemical processes in the chemical industry. This value was chosen to represent a reasonable upper limit that encompasses the vast majority of chemical processes found in the chemical industry[^7]. However, there are some processes that use temperatures greater than 1500 K (e.g., flue dust gasification, industrially known as the Koppers-Totzek process). Changing the upper limit of temperature only affects the slope of the shaded area in Figure 6 from the main text; e.g., using 2000 K or for an upper limit only extends the shaded region marginally (Figure S8). In this work, the limit of 1500 K is not meant to be a hard limit dividing what is possible and not possible for temperature to drive a chemical reaction. Instead, 1500 K is meant to provide a reasonable guide and ground the analysis with real temperatures; if a chemical reaction is just outside of the shaded region, this does not imply it cannot be driven with temperature, only that the temperature necessary would be large and needs to be taken into consideration when designing a process.

It is important to note that for the sake of generality, we have used the equilibrium constant exclusively as a metric for determining whether a reaction can be driven at a certain set of operating conditions. In practice, it is possible to drive reactions at conditions that would appear untenable from a simple thermodynamic plot through engineering ingenuity and system design. For example, by removing one of the products, one can leverage Le
Chatelier’s principle to help drive a reaction and push the equilibrium toward a desired product. This is leveraged in solar thermal water splitting and carbon dioxide splitting at temperatures ranging from 1000 K to 1500 K where the oxygen product is incorporated into the metal oxide catalyst in a multi-step process, leading to an equilibrium shift that favors hydrogen or carbon monoxide in the cases of water splitting and carbon dioxide reduction, respectively.\cite{8,9} Other common uses for this technique include the removal of water to enable dehydration reactions, and reactive distillation systems. Despite this, in general the equilibrium constant represents a very good proxy for thermodynamic feasibility with the caveat that careful system engineering can help drive reactions when thermodynamic operating conditions indicate a reaction is infeasible.

S9 Simple Descriptors

Some of the major points about reaction feasibility and thermodynamic equilibrium can be determined from simple descriptors without the need for our non-dimensionalization scheme. For example, simply looking at the sign of $\Delta G_{\text{rxn}}$ at a given temperature will tell us whether the reaction is thermodynamically favorable, and $T_{\text{char}} = \Delta H_{\text{rxn}}^0 / \Delta S_{\text{rxn}}^0$ provides us with a metric of whether temperature alone can drive a given reaction to thermodynamic equilibrium. Other potential descriptors such as $\sum_i \nu_i$ for a reaction tell us the influence of pressure and $E_{\text{eq}} = \Delta G_{\text{rxn}} / nF$ gives an idea of how much voltage is necessary to drive the reaction. Individually, each of these descriptors is extremely useful, but they unfortunately must be calculated for each specific reaction, often at various operating conditions. These descriptors are therefore useful, but do not contain the same amount of information as our visualization in Figure S6. As an example, using $\Delta G_{\text{rxn}}$ and $T_{\text{char}}$ as descriptors, we have plotted the same data as in Figure S6 on new axes (Figure S9). While discrimination via these quantities can tell us whether a reaction is capable of being driven by temperature to equilibrium conversion, they do not provide information about the magnitude of the influence of temperature, pressure, and voltage, and they do not provide any information on the
influence of pressure on the reaction. When temperature, pressure, and voltage deviate from ambient conditions, the new equilibrium conversion is readily apparent on Figure S6 as the axes scale with these thermodynamic quantities as discussed in the main text. Additionally, the influence of pressure on a reaction can be quickly ascertained on our axes based on the y-value of the point (or explicitly shown in Figure S6 with the vertical lines), whereas the role of pressure is difficult to determine from the Gibbs free energy of reaction or the equilibrium temperature. Because our axes allow for quantification of the influence of thermodynamic parameters on the equilibrium conversion, our axes can be used to investigate such questions as: what is the equilibrium conversion of ammonia synthesis at operating conditions? And: which reactions can rely on pressure to increase equilibrium conversion at conditions which facilitate fast kinetics? The answers to these questions are not novel—we could easily gather additional descriptors similar to those mentioned above that would encompass more aspects of the system. However, with our carefully chosen non-dimensional scheme, we can visualize all of these descriptors on a single plot for multiple reactions instead of requiring a list of descriptors for each individual reaction at every temperature, pressure, and voltage of interest. We can also add and subtract reactions on our proposed axes for simple exploration of possible reactants and products as discussed in the main text.

Figure S9: Transformation of Figure S6 data to potential binary descriptors as axes. Although some of the information is preserved on these axes, there is a significant loss of information as described in SI Appendix, Discussion 8.
Supplemental References

References


