The Thermodynamics of Irreversible Processes

Consider the following thermodynamic system, which is divided into two sides (1 & 2) by a membrane containing pores through which molecules of some substance, A, can pass. This system would thus be analogous to a cell separated from the extracellular space by its plasma membrane, with A representing some solute such as Na\(^+\), K\(^+\), or Ca\(^++\), and the pores representing ion channels. Let’s put \(n_{A1}\) & \(n_{A2}\) moles of A in Side 1 and Side 2, respectively.

<table>
<thead>
<tr>
<th>Side 1</th>
<th>Side 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n_{A1})</td>
<td>(n_{A2})</td>
</tr>
<tr>
<td>(\mu_{A1})</td>
<td>(\mu_{A2})</td>
</tr>
<tr>
<td>(\text{dn}_A)</td>
<td></td>
</tr>
</tbody>
</table>

The contribution of \(n_i\) moles of substance A to the chemical potential in any system is given by:

\[
\mu_i = \mu^* + RT \ln(n_A), \quad \text{Equation 1}
\]

where \(\mu^*\) is a standard state chemical potential that can’t be calculated or determined (since we’re going to be interested in gradients or changes in chemical potential from one place or state to another, \(\mu^*\) will ‘drop out’ of any calculations we do, so don’t worry about it). For our system, the chemical potential due to \(n_{A1}\) moles of A in Side 1 will be:

\[
\mu_{A1} = \mu^* + RT \ln(n_{A1}).
\]

Similarly, for Side 2 we have:

\[
\mu_{A2} = \mu^* + RT \ln(n_{A2}).
\]

Now, let’s allow \(\text{dn}_A\) moles of A move from side 1 to side 2, and see if we can learn anything of interest.

Remember that Gibbs Free Energy change associated with the movement of matter is \(\mu \text{d}n\), and that the sum of the Gibbs Free Energy changes (\(= \sum \mu \text{d}n\) when only movement of matter is involved) must be \(\leq 0\) for all spontaneous processes. In this case, nothing is changing except for the amount of A in Side 1 and Side 2 (i.e., \(dP = dT = dV = 0\)). This lets us write the expression for the total Gibbs Free Energy change accompanying the movement of matter from Side 1 to Side 2 as:

\[
dG = \sum \mu_{Ai} \text{d}n_{Ai} = \mu_{A1} \text{d}n_{A1} + \mu_{A2} \text{d}n_{A2} \leq 0 \quad \text{Equation 2}
\]

with the equality applying only to the equilibrium situation.

Let’s now work with only the right-hand part of Equation 2, i.e.:

\[
\mu_{A1} \text{d}n_{A1} + \mu_{A2} \text{d}n_{A2} \leq 0
\]
Since $dn_{A2} = -dn_{A1}$ (because whatever leaves Side 1 has to enter Side 2), it’s easy to show, by substituting

$-dn_{A1}$ for $dn_{A2}$ in the previous expression, that:

$$(\mu_{A1} - \mu_{A2})dn_{A1} \leq 0 \quad \text{Equation 3}$$

for all processes. Let’s explore what Equation 3 is telling us.

Consider the situation in which $\mu_{A1} > \mu_{A2}$. The quantity $(\mu_{A1} - \mu_{A2})$ will thus be positive ($> 0$), and in order for Equation 3 to be true, $dn_{A1}$ must be $< 0$. As you’ll recall from your calculus class, a negative value for $dn_{A1}$ means that the amount of A in Side 1 is decreasing. In other words, molecules of A will leave Side 1 and enter Side 2. What if $\mu_{A2} > \mu_{A1}$? Well, you should now be able to show that this would require $dn_{A1} > 0$, meaning that A would leave Side 2 and enter Side 1. By extension (meaning: the math breaks down), if $\mu_{A1} = \mu_{A2}$ there will be no net flux of A. Let’s put these results in tabular form:

<table>
<thead>
<tr>
<th>Condition</th>
<th>Requires:</th>
<th>Direction of Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{A1} &gt; \mu_{A2}$</td>
<td>$dn_{A1} &lt; 0$</td>
<td>Side 1 $\rightarrow$ Side 2</td>
</tr>
<tr>
<td>$\mu_{A1} &lt; \mu_{A2}$</td>
<td>$dn_{A1} &gt; 0$</td>
<td>Side 2 $\rightarrow$ Side 1</td>
</tr>
<tr>
<td>$\mu_{A1} = \mu_{A2}$</td>
<td>n/a</td>
<td>No net flux; equilibrium</td>
</tr>
</tbody>
</table>

These results are extremely important and are the main reason that we spend so much time talking about thermodynamics at the start of the semester. The significance of those results, which cannot be overstated, can be summed up as follows:

**Matter tends to move from regions of high chemical potential toward regions of low chemical potential, and it is gradients in chemical potential -- not just concentration gradients -- that are really the driving force for flux of matter from place to place.**

The reason that this conclusion is so very important to a budding physiologist such as yourself is because $\mu$ depends on a number of parameters of a given system, not just on the amount of matter it contains. I.e.,

$$\mu = f(n, T, P, V, \psi, \text{ etc. } ).$$

By extension,

$$\Delta \mu = f(\Delta n, \Delta T, \Delta P, \Delta V, \Delta \psi, \text{ etc. }).$$

In other words, a gradient in $\mu$ ($d\mu$) can result from gradients in $n$, $T$, $P$, $V$, $\psi$, or a combination of any of them.

The $d\psi$ term is really important, because it means that gradients in electric potential (i.e., potential differences between two points) can contribute to chemical potential gradients. This
implies -- and we’re going to see this later -- that a gradient in $\psi$ ($= \Delta \psi$) can actually offset a concentration gradient and, if $\Delta \psi$ is big enough, we can actually have matter moving against its concentration gradient and large concentration gradients being maintained at equilibrium.

Pretty bizarre............