Lecture 13 – Chapter 16, Sections 1-2
Equilibrium

- Reversible reactions
- Dynamic Equilibrium
- Equilibrium Constant
- Pure materials, solvents
First, Exam summary

<table>
<thead>
<tr>
<th>Grade</th>
<th>Count</th>
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</thead>
<tbody>
<tr>
<td>High</td>
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</tr>
<tr>
<td>Mean</td>
<td>65.6</td>
</tr>
<tr>
<td>90s</td>
<td>3</td>
</tr>
<tr>
<td>80s</td>
<td>3</td>
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<tr>
<td>70s</td>
<td>8</td>
</tr>
<tr>
<td>60s</td>
<td>16</td>
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<tr>
<td>50s</td>
<td>15</td>
</tr>
<tr>
<td>≤ 50</td>
<td>3</td>
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Reactions are never one-way

- Remember from chapter 14 if $\Delta G < 0$ reaction is spontaneous as written
- But if $\Delta G > 0$ reaction is spontaneous in opposite direction

- Thus, it is ALWAYS possible for reactions to go in either direction

- ALL REACTIONS ARE REVERSIBLE
Example

• Last chapter we saw $2 \text{NO}_2 \rightarrow \text{N}_2\text{O}_4$
  – Rate = $k_f[\text{NO}_2]^2$
• This can just as well be $\text{N}_2\text{O}_4 \rightarrow 2 \text{NO}_2$
  – Rate = $k_b[\text{N}_2\text{O}_4]$
If there is lots of NO$_2$ and just a little N$_2$O$_4$, which reaction is probably faster?

<table>
<thead>
<tr>
<th>33%</th>
<th>1. Forward 2 NO$_2$ $\rightarrow$ N$_2$O$_4$</th>
</tr>
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<tbody>
<tr>
<td>33%</td>
<td>2. Back N$_2$O$_4$ $\rightarrow$ 2 NO$_2$</td>
</tr>
<tr>
<td>33%</td>
<td>3. They are the same</td>
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If there is lots of $\text{N}_2\text{O}_4$ and just a little $\text{NO}_2$, which reaction is probably faster?

33% 1. Forward $2 \text{NO}_2 \rightarrow \text{N}_2\text{O}_4$

33% 2. Back $\text{N}_2\text{O}_4 \rightarrow 2 \text{NO}_2$

33% 3. They are the same
Dynamic Equilibrium

- At some point the forward rate and back rate will be equal

- This is dynamic equilibrium
  - Product and reactant are both being produced and consumed at equal rates.
  - Concentrations are constant
Equilibrium constant

- At equilibrium both reactant and product are present
- Rates are equal
- Ratio of rate constants called the Equilibrium Constant

\[
\frac{k_f}{k_b} = \frac{\left[N_2O_4\right]_{eq}}{\left[NO_2\right]_{eq}^2}
\]

\[
K_{eq} \equiv \frac{k_f}{k_b} = \frac{\left[N_2O_4\right]_{eq}}{\left[NO_2\right]_{eq}^2}
\]
Equilibrium constant

- In general for a reaction like
  \[ aA + bB \rightarrow dD + eE \]

\[
K_{eq} = \frac{[D]_{eq}^d [E]_{eq}^e}{[A]_{eq}^a [B]_{eq}^b}
\]

Look familiar? \( K_{eq} \) is just \( Q \) when at equilibrium
A few details…

• Remember that $Q$ is unitless – so is $K_{eq}$
  – Each concentration (or pressure) is implicitly divided by the standard concentration (1 M) or pressure (1 bar or 1 atm)

$$K_{eq} = \frac{\frac{p_{N_2O_4}}{1 \text{ bar}}}{\left(\frac{p_{NO_2}}{1 \text{ bar}}\right)^2}$$
A few more details…

• Pure substances (liquids or solids) **by definition** have a concentration of 1
  – Concentrations are the same before and after reaction

• Solvents also have a concentration of 1.
  – Technically we use mole fraction
  – Solvent mole fraction always approx. 1
  – Again amount of solvent is effectively unchanged
Today
• CSI your exam
• Plan to attend Neckers (Fri) / HHMI (Thurs) seminars

Thursday
• Keypad clinic
  – Noon SC1019

Friday
• Read Chapt 16
• Neckers lecture