QUIZ NEXT WEEK

- Monday is a holiday
  - Tues LT2
  - Wed LT3
  - Thurs LT3
  let me know if you can’t make it

- Topics
  - Kinetics
  - Equilibrium
  - Acids & Bases

- Don’t forget to bring a calculator
Thermodynamics I

Silberberg 2nd Ed, Chapter 20
Any questions or requests - email to c.kepert@chem.usyd.edu.au
Why Chemical Reactions Occur

Recall the Following:

\[ K_c \propto e^{-\Delta H^0/RT} \]

- Endothermic reaction lies more to right at higher \( T \)
  - according to this picture, we might expect a 50:50 mix of reactants and products at very high temperature.

**BUT:** Boiling water is an endothermic process. At high temperature we can convert all of the liquid into vapour - HOW IS THIS POSSIBLE?
Why Chemical Reactions Occur

- While most exothermic reactions ($\Delta H < 0$) are spontaneous, some endothermic ones ($\Delta H > 0$) are also spontaneous.
- *Entropy* ($S$) is also important.
- Entropy depends on how random a system is.

Mixing is spontaneous even though there is no energy change.
Entropy (S)

• Entropy is a measure of the randomness or disorder.
  – *The natural progression is from an ordered to a disordered state.*

• Entropy is a thermodynamic quantity that describes the *number of arrangements that are available to the system in a given state.*
  – *In nature, processes proceed spontaneously towards the states with the highest probability of existing.*

• The main concept here is the more ways a particular state can be achieved the greater is the likelihood of finding it in that state.
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- More ways to arrange black and white balls when mixed than when separate.
- The black and white balls have more "freedom" if they can move around the entire system.

Entropy ($S$)

• Similarly, a gas is more probable than a solid:

- Gas molecules have more "freedom" than molecules in solid.
Recap

- The *system* - the portion of the universe being studied (usually the chemical reaction)
- The *surroundings* - everything that is outside the system (usually the immediate surroundings to the chemical reaction)
- The *universe* - the system + the surroundings

**First Law of Thermodynamics (Law of Conservation of Energy):**

\[
\Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0
\]

- the energy of the universe is constant.
Second Law Of Thermodynamics

• In a spontaneous process the entropy of the universe must increase:

\[ \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 \]

- the Universe becomes more disordered
Third Law of Thermodynamics

At 0 K, all substances have the same entropy

(the “baseline” for entropy – define this as $S = 0$)

e.g., a perfect crystal has zero entropy at absolute zero.

Ice

Insulin grown in zero gravity (space)
Entropy Change of Dissolution/Precipitation
**Entropy Change of Dissolution/Precipitation**

**Dissolving solids in liquids**
- the entropy of the atoms in the crystal *increases* as the atoms become more disordered & have higher freedom
- the entropy of the molecules in the liquid *decreases* as they become organised around the dissolved species

**Dissolving gases in liquids**
- the entropy of the atoms in the gas *decreases* as the atoms become less disordered & have lower freedom
Dissolution/Precipitation Demonstrations

\[ \Delta H < 0 \quad \Delta S < 0 \]
\[ \Delta H > 0 \quad \Delta S > 0 \]

Generally true

Precipitation

Dissolution
Entropy: Qualitative

- More Disorder → Higher $S$

- For given substance: $S_{\text{gas}} > > S_{\text{liquid}} > S_{\text{solid}}$

- Same substance: higher $T \rightarrow$ higher $S$
### Entropy: Quantitative

**Two similar substances: more complex molecule has higher $S$**

- e.g. at 298 K:

<table>
<thead>
<tr>
<th></th>
<th>$S^\circ / J \text{ K}^{-1} \text{ mol}^{-1}$</th>
<th></th>
<th>$S^\circ / J \text{ K}^{-1} \text{ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O (l)}$</td>
<td>70</td>
<td>$\text{CH}_4 (g)$</td>
<td>186</td>
</tr>
<tr>
<td>$\text{H}_2\text{O (g)}$</td>
<td>189</td>
<td>$\text{CH}_3(\text{CH}_2)_3\text{CH}_3 (g)$</td>
<td>388</td>
</tr>
<tr>
<td>$\text{H}_2\text{S (g)}$</td>
<td>206</td>
<td>$\text{C(CH}_3)_4 (g)$</td>
<td>306</td>
</tr>
</tbody>
</table>

**Diagrams**

- NO
- NO$_2$
- N$_2$O$_4$
Entropy Of Reaction

Entropies in reactions can be added & subtracted in the same way as enthalpies (Hess’ Law)

- Calculate $\Delta S^\circ_{\text{rxn}}$ for the formation of urea

$$2\text{NH}_3 (g) + \text{CO}_2 (g) \rightleftharpoons \text{NH}_2\text{CONH}_2 (aq) + \text{H}_2\text{O} (\ell)$$

$S^\circ$: $2 \times 193$  214  174  70 J mol$^{-1}$ K$^{-1}$

$$\Delta S^\circ_{\text{rxn}} = \Sigma S^\circ_{\text{products}} - \Sigma S^\circ_{\text{reactants}}$$

$$\Delta S^\circ_{\text{rxn}} = [(174 + 70) - (2 \times 193 + 214)]$$

$$= -356 \text{ J mol}^{-1} \text{ K}^{-1}$$

We would expect $\Delta S^\circ < 0$ Why?
Examples

1. Predict the sign of $\Delta S_{\text{sys}}$ for following processes:
   - **Alcohol evaporating:**
     - Goes from liquid to gas (vapour),
     - $\Delta S_{\text{sys}} = S(\text{gas}) - S(\text{liquid}) > 0$
   - **Lake freezing in winter**
     - Goes from liquid to solid,
     - $\Delta S_{\text{sys}} = S(\text{solid}) - S(\text{liquid}) < 0$

2. Arrange in order of decreasing standard molar entropy, $S^\circ$, $\text{ClO}_4^-$, $\text{ClO}_2^-$, $\text{ClO}_3^-$
   - More complex has higher entropy, so $S^\circ$ values go
     - $\text{ClO}_4^- > \text{ClO}_3^- > \text{ClO}_2^-$
H₂ (g) + ½ O₂ (g) → H₂O (l)

ΔS° = −163 J K⁻¹ mol⁻¹
ΔH° = −285 kJ mol⁻¹

• Decrease in entropy of system:
  ΔS°_reaction = ΔS°_system < 0

• Reaction is spontaneous
∴ +ve total entropy change (system + surroundings)
⇒ ΔS_surroundings increases more than ΔS_system decreases
  ΔS_system + ΔS_surroundings > 0

• Entropy change to surroundings is a result of the heat released by the reaction (it’s exothermic)
Reaction Spontaneity: Evaluating $\Delta S_{\text{surroundings}}$

$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\ell)$

$\Delta S^0 = -163 \ \text{J K}^{-1} \ \text{mol}^{-1}$

$\Delta H^0 = -285 \ \text{kJ mol}^{-1}$

- Energy released by the reaction randomises the surroundings

\[
\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{reaction}}}{T}
\]

**Second Law**: for a spontaneous reaction we need

$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \Delta S_{\text{system}} - \Delta H_{\text{system}}/T \ > \ 0$

Spontaneity depends both on entropy *and* enthalpy
Gibbs “Free Energy”

\[ G = H - TS \]

Because a spontaneous reaction maximises \( S_{\text{universe}} \), it also minimises \( G \)

Free Energy is the driving force for chemical reactions!
It is a combination of enthalpic and entropic effects.

Spontaneous reactions minimise free energy

To be learnt