The role of $\Delta S$ in colligative properties

Absolute entropies

Entropy change of reaction

$\Delta S = \frac{\Delta H}{T} = -\frac{\Delta H}{T}$

The role of $\Delta S$ in colligative properties

$\Delta S$ and freezing point depression

Make a diagram of $S$ (vertical axis) for liquid and solid water (ice).

Connect the two entropies with an arrow corresponding to liquid $\rightarrow$ solid.

What is the length of the arrow?

$\Delta S$ and freezing point depression

How is $S$(liquid) changed by adding a small amount of solute?

What must happen to the length of the arrow connecting the water solution to pure ice?

How can this change come about?
Entropy change of reaction, CH102 Spring 2016, A1 and A2

lecture 30

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$\Delta S$ and freezing point depression

$\Delta S$ and colligative properties

Each of the four colligative properties can be understood in terms of entropy changes.

See the notes on colligative properties at ...

http://quantum.bu.edu/courses/ch102-spring-2016/handouts.html

How to determine $\Delta S_{sys}$ for a chemical reaction?

We can get $\Delta S_{sys}$ by analyzing changes in particle and energy dispersal in the system.

But, in practice, it is easier to get $\Delta S_{sys}$ by measuring heat flow between system and surroundings when they are in equilibrium.

At equilibrium, $\Delta S_{sys} = 0$, and so ...

$\Delta S_{sys} = -\Delta S_{sol} = -\Delta H_{sol}/T = +\Delta H_{sys}/T$

How to determine $\Delta r S^\circ$? 

At equilibrium, $\Delta S_{sys} = 0$, and so ...

$\Delta S_{sys} = -\Delta S_{sol} = -\Delta H_{sol}/T = +\Delta H_{sys}/T$

At 0 K, for each substance $W = 1$ and so $S = 0$!

Therefore, by heating, we can find $S$ for each substance at a particular temperature.

These values are called absolute entropies.
Find S at a particular temperature

Make a sketch of how you expect the entropy of water to change with temperature, starting from $S = 0$ at $T = 0$ K and ending at the entropy at $T = 400$ K.

$S(400 \text{ K}) = S(\text{heating solid}) \ldots$  
$+ \frac{\Delta H_{\text{fus}}}{T_{\text{fus}}} \ldots$  
$+ S(\text{heating liquid}) \ldots$  
$+ \frac{\Delta H_{\text{vap}}}{T_{\text{vap}}} \ldots$  
$+ S(\text{heating gas})$

Entropies typically are tabulated at 298 K.
Called standard entropies, $S^\circ$
Note, these absolute entropies, not entropy changes
How to get entropy change of reaction, $\Delta_r S^o$?
1. Get absolute entropies $S^o$
2. $\Delta_r S^o = S^o_{\text{products}} - S^o_{\text{reactants}}$

Entropy change of reaction, $\Delta S^o_{\text{rxn}}$

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

Rules of thumb:
- If more gas moles formed, $\Delta S^o$ large and positive
- If more gas moles consumed, $\Delta S^o$ large and negative
- If gas moles unchanged, $\Delta S^o$ small but positive or negative

\[
\begin{align*}
\Delta_r S^o = S^o_{\text{products}} - S^o_{\text{reactants}} \\
2 \text{Zn(s)} + \text{O}_2(g) &\rightarrow 2 \text{ZnO(s)} \\
\Delta_r S^o &= 2 \times 43.7 - (2 \times 41.6 + 205.0) = -200.8 \text{ J/K} \\
\Delta n_g &= -1, \text{ so } \Delta_r S^o \text{ is large and negative} \\
\text{N}_2(g) + \text{O}_2(g) &\rightarrow 2 \text{NO(g)} \\
\Delta_r S^o &= 2 \times 210.8 - (191.6 + 205.0) = +25 \text{ J/K} \\
\Delta n_g &= 0, \text{ so } \Delta_r S^o \text{ is small}
\end{align*}
\]