Lecture 13  Chapter 7 sections 1-9

Announce:

Outline

ΔS at constant V (or P)
ΔS at constant T
ΔS of mixing
Third Law of Thermodynamics (S at low T)
S of phase transitions
Standard Molar Entropy
Molecular (statistical) entropy

Quick Review

Boltzmann definition of entropy

\[ S = k \ln W \]

Entropy from molecular perspective, (from Boltzmann)

\[ S = kT \left( \frac{\partial \ln Q}{\partial T} \right) + k \ln Q \]

ΔS of a constant V process (const P just changes Cv to Cp)

\[ \Delta S = C_v \ln \left( \frac{T_f}{T_i} \right) = nC_v \ln \left( \frac{T_f}{T_i} \right) \]

Which has gotten us into chapter 7:

We just wrote this down. Remember **we assumed what in the derivation?** constant Cv

\[ \Delta S = C_v \ln \left( \frac{T_f}{T_i} \right) = nC_v \ln \left( \frac{T_f}{T_i} \right) \]

So, **when T increases, S?** increases and large \( C_v \) amplifies the effect.

**What about a constant pressure process?** \( dq \) is \( dH \), so \[ \Delta S = nC_p \ln \left( \frac{T_f}{T_i} \right) \]

All right then, that was simple. Let’s move on to \( P \) and \( V \) not constant.

**Reversible Isothermal expansion**

Draw familiar expanding piston with thermostat
What does isothermal allow us to say about entropy? $q = -w$.

So, then what about $dS$? $dS = dq/T = P_{\text{ext}} \, dV/T$

$$
\Delta S = \int_{V_i}^{V_f} \frac{P_{\text{ext}} \, dV}{T} = \int_{V_i}^{V_f} \frac{nRT \, dV}{VT} = nR \int_{V_i}^{V_f} \frac{dV}{V} = nR \ln \left( \frac{V_f}{V_i} \right)
$$

also for an ideal gas, $P_i/P_f = V_f/V_i$, so $\Delta S = nR \ln (P_i/P_f)$

The bottom line? as $V$ increases (or $P$ decreases) then $S$ increases

**Entropy of Mixing**

Recall the thing I drew last Friday

We have two ideal gasses at the same $T$ and $P$ in separate containers of volumes $V_1$ and $V_2$. We already talked about $\Delta U = 0$ and $\Delta H = 0$ for opening the stopcock. What about $\Delta S$?

$$
\Delta S = nR \ln (V_f/V_i)
$$
For gas A, what is $V_1$?  $V_1 + V_2$. So, $\Delta S_A = n_A R \ln( (V_1 + V_2) / V_1 )$

of course, for gas B this becomes $\Delta S_B = n_B R \ln( (V_1 + V_2) / V_2 )$

Total entropy of mixing, then, $\Delta_{Mix} S = n_A R \ln( (V_1 + V_2) / V_1 ) + n_B R \ln( (V_1 + V_2) / V_2 )$

But for ideal gases, $V_1 / (V_1 + V_2) = n_A / (n_A + n_B) = X_A$ (mole fraction)

So, $\Delta_{Mix} S = n_A R \ln(1 / X_A) + n_B R \ln(1 / X_B) = -R (n_A \ln X_A + n_B \ln X_B)$

What values does $X$ take?  always between 0 and 1
Therefore what values does $\Delta_{Mix} S$ take?  always positive!!!!!

This makes sense because there must always be an increase in the number of configurations when two things mix.

3rd Law of Thermodynamics
As long as we are on entropy, we should define reference states.
The third law says that the entropy of a perfectly crystalline pure element at a temperature of absolute zero is zero.
In other words, it is impossible to reach absolute zero.

Recall from our molecular picture of entropy provided by Boltzmann, that?
$S = k \ln W$
and $W$ at absolute zero for a perfectly ordered substance is 1.

Now, a corollary of this that isn’t so obvious is that $C_p \to 0$ as $T \to 0$.
Recall the shape of the $C_{vib}$ vs. $T$ curve:
Why does C get small as T gets small? because kT gets much smaller than the vibrational energy spacing. Because? at low enough T only the ground state is available. So, what would a plot of the translational contribution to the heat capacity look like? Same thing. Even translational spacing is large at some temp.

Entropy of phase transitions

Phase transitions are accompanied by a large change in molecular order, so what would we expect for entropy? Also a large change.

Consider a system at equilibrium at its transition temperature (i.e. water 373 K). The transfer of heat must be reversible in this instance (because of equilibrium). So, \( dS = dq_{\text{transition}} / T \).

What is \( dq \)? const. pressure so \( dq = dH \).

Finally then

\[
\Delta_{\text{trans}}S = \Delta_{\text{trans}}H / T_{\text{trans}}
\]

This is generally true for constant pressure phase transitions. What is \( \Delta H \) for vaporization? greater than zero, so \( \Delta S_{\text{vap}} \) is greater than zero – makes sense because gas phase has greater disorder than liquid phase. So the sign of \( \Delta S \) for condensation? negative! This is OK because \( \Delta S \) for the surroundings is positive.

One other general note is that \( \Delta_{\text{vap}}S \) is around 85 J/(Kmol) for most things that are liquids at room temp. This is called? Trouton’s rule. This is true because most things are very similar in gas phase, and the amount of disorder in liquid phase is also about the same. Notable exception? water – strong H-bonding makes its liquid disorder quite different.

As example of how to tie all of this entropy stuff together, let’s heat water from 90 to 110 degrees C and calc the entropy change.

\( \Delta S \) for \( \text{H}_2\text{O} \) (l) \( \rightarrow \) \( \text{H}_2\text{O} \) (g) for \( T_1 = 90 \) C and \( T_2 = 110 \) C?

\[
\Delta S = nC_{p,m}(\text{H}_2\text{O},l) \ln \left( \frac{373 \text{ K}}{T_1} \right) + \frac{\Delta_{\text{vap}}H(\text{H}_2\text{O})}{373 \text{ K}} + nC_{p,m}(\text{H}_2\text{O},g) \ln \left( \frac{T_2}{373 \text{ K}} \right)
\]

As a quick aside: At a phase transition, what is \( C_p \)?

\[
C_p = \left( \frac{\partial H}{\partial T} \right)_p \quad (H \text{ changes while } T \text{ is constant at phase transition, so } C_p \text{ is infinite})
\]

Calculating Standard Molar Entropies from Thermodynamic Data
Entropies are often measured by heat capacity measurements to near absolute zero.

\[ S(T) = S_0 + \int_0^T \frac{C_p dT}{T} \]

Of course the third law tell us? \( S_0 \) is 0 for pure crystalline elements.

**In other words, the entropy of a substance at temperature \( T \) is evaluated by calculating the area under a plot of \( C_p/T \) vs. \( T \)**

These measurements are often called “Third Law” entropies (\( S^o \)). Tables usually list the values for this quantity at 298 K.

Of course, these entropies can be calculated just like any other state function. We won’t do an example here, but it follows the general rule:

\[ \Delta_v S = S_0(\text{products}) - S_0(\text{reactants}) \]

Example:

\[ \text{H}_2 \ (g) + \frac{1}{2} \text{O}_2 \ (g) \rightarrow \text{H}_2\text{O} \ (l) \text{ at 298 K} \]

\[ \Delta_v S^o = S^o(\text{H}_2\text{O}, \ l) - [S^o(\text{H}_2, \ g) + \frac{1}{2} S^o(\text{O}_2, \ g)] \]

\[ \Delta_v S^o = -163.3 \text{ J K}^{-1} \text{ mol}^{-1} \ (a \ big \ decrease \ in \ entropy \ because \ of \ the \ formation \ of \ a \ liquid \ from \ the \ gases) \]

And finally, we always want to get back to a detailed, molecular picture:

**Calculating Statistical Standard Molar Entropies**

recall our relationship between entropy and the partition function

\[ S = k \ln Q + kT \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} \]

**Diatomic Case:**

How do we expect trans, rot, vib, elec parts of entropy to combine (addition, multiplication, subtraction)? Addition, just like energy

\[ S = S_{\text{trans}} + S_{\text{rot}} + S_{\text{vib}} + S_{\text{elec}} \]

So, then:
\[ S = R \ln \left( \frac{2\pi nkT}{h^2} \right)^{3/2} \left( \frac{Ve^{5/2}}{N_A} \right) - \ln(1 - e^{-\Theta_{rot}/T}) + \ln \left( \frac{\Theta_{vib}}{e^{\Theta_{vib}/T} - 1} \right) + \ln (1 - e^{-\Theta_{elec}/T}) \]

Notice how this lets us see how each of the molecular descriptors affects entropy.

For \( \text{N}_2 \) at 298 K (\( \Theta_{rot} = 2.88 \text{ K} \), \( \Theta_{vib} = 3374 \text{ K} \), \( g_{elec} = 1 \) and \( V_m = 24.5 \text{ L mol}^{-1} \)):

\[ S^o = 150.4 + 41.13 + 0.00115 + 0 = 191.5 \text{ J K}^{-1} \text{ mol}^{-1} \]

The individual contributions to entropy correlate directly with the values of the individual partition functions (a larger partition function indicates greater entropy!)

Notice how things like mass, \( V \), \( \Theta_{rot} \), \( \Theta_{vib} \) effect entropy. Explain this table:

<table>
<thead>
<tr>
<th>Compound</th>
<th>( S^o ) (J K(^{-1}) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2\text{H}_2 )</td>
<td>200.9 (lighter than ( \text{N}_2 ), yet higher entropy)</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td>219.6</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_6 )</td>
<td>229.6</td>
</tr>
</tbody>
</table>

large mass should give large entropy, but rotations also important. Vibrations may be important, but their effect tends to be small at room temp unless molecules have many many vibrational modes. Also notice that rotatable bonds is part of vibrational contribution.