Lecture 12  Chapter 6 sections 5-9 with bonus Chapter 7 material

Announce:
Review quizzes briefly. 
Because \( T \ll Q_{VIB} \), \( C_{v, vib} \) is 0
adiabatic, so \( q = 0 \) (most got that), and \( \Delta U = w \) (most got that).
But many tried to say \( w = -nRT \ln \left( \frac{V_f}{V_i} \right) \) instead of \( \Delta U = \int C_v \, dT \)

**Remember how that expression is derived?** By plugging \( P = \frac{nRT}{V} \) into

\[ w = \int p_{ext} \, dV \, . \] Since \( T \) is not constant, you can’t do the integral. **The moral of the story?** BEWARE EQUATION SHEETS

**Outline**
Statistical Entropy
\( S \) relation to \( Q \)
\( S \) changes with \( T \)
\( S \) changes with \( P \) and \( V \)

**Quick Review**

1\(^{st}\) law deals with energy conservation – tells us whether a process is permissible
2\(^{nd}\) law deals with spontaneity – tells us whether a process will happen (spontaneously)

Carnot cycle:

\[ 1 \quad \text{Isotherm} \ T = T_1 = T_2 \]
\[ 4 \quad \text{Isotherm} \ T = T_1 = T_3 = T_4 \]

\[ IV \quad \text{adiabat} \]
\[ III \quad \text{adiabat} \]

\[ P \ (\text{atm}) \]
\[ V \ (\text{L}) \]

Remember we filled out the table of \( q \), \( w \), and \( \Delta U \) for each step in the process.
\( \Delta U \) for the full cycle? 0 because it’s closed.

efficiency was work out over heat in \( - \frac{w}{q_h} \)
\[ \sum q_{rev}/T \] was 0 over the full cycle \( \rightarrow \) a state function. We define this as entropy – \( S \). Principle of Clausius: \( dS \geq dq/T \)

OK, let’s move into today’s stuff! Remember that we are always looking for connections to molecular descriptions. So, we will do this for Entropy.

**Statistical entropy:**

We have covered Boltzmann before. **What did he say?**

\[
p_j = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}
\]

This a crucial statement, however, his epitaph says \( S = k \ln W \)

\( W \) is the disorder in our system – the \# of configurations of the ensemble that are possible at a particular \( E \).

Remember back from a couple weeks ago when we were flipping coins and talking about probability. We came up with a formula for the probability of getting some number of heads out of some number of flips. **anyone recall?**

\[
P(N,h) = \frac{N!}{h!(N-h)!} \frac{2^N}{N!}
\]

Remember the numerator is the total \# of combinations of \( h \) heads and \( N-h \) tails in \( N \) flips. We defined this as the weight \( W(N,h) = \frac{N!}{h!(N-h)!} \)

**Anyone see a connection?** Two \( W \)s, each stands for \# of configurations in a system. **What about when we had dice, anyone recall what \( W \) was for this?**

\[
W = \frac{N!}{n_1!n_2!n_3!n_4!n_5!n_6!}
\]

Remember that \( N \) is the total \# of dice we are rolling, \( n_1 \) is the \# of dice that land on 1 (i.e. are in state 1), \( n_2 \) is the \# of dice in state 2, etc.

Now let’s transfer these ideas to molecules. Using the book’s nomenclature, \( A \) is the number of systems in the ensemble. \( a_j \) are number of systems in state \( j \). So, in these terms, **what is \( W \)?**

\[
W = \frac{A!}{a_0!a_1!a_2!a_3!\cdots a_j!}
\]

**Then what is \( S \)?**
\[ S_{\text{ensemble}} = k \ln W = k \ln \left( \frac{A!}{a_0!a_1!a_2! \ldots} \right) = kA \ln A - k \sum_j a_j \ln a_j \]

The last step makes use of lots of algebra and Stirling’s approx (very important), which says \( \ln N! \approx N \ln N - N \)

What does this equation mean? It says that more ways to arrange a system (big \( W \)) gives large entropy. Note that if we are at absolute zero, what should \( W \) be? Well, \( A \) is \( A \) and \( a_0 = A \) and \( a_1 = a_2 = \ldots = 0 \). This means \( W \) is 1, because all of the system are in the lowest state. So what is the entropy? 0 – makes sense. We’ll come back to this.

Let’s work with the above a little bit: Notice that \( A = \sum a_j \)

\[ S_{\text{ensemble}} = k \sum_j (a_j \ln A - a_j \ln a_j) \quad \text{group together log terms} \]

\[ S_{\text{ensemble}} = -k \sum_j a_j \ln \left( \frac{a_j}{A} \right) \quad \text{now substitute} \ a_j = p_j A \]

\[ S_{\text{ensemble}} = -k \sum_j p_j A \ln p_j \]

\[ S_{\text{ensemble}} = -kA \sum_j p_j \ln p_j \quad \text{now divide through by} \ A \]

\[ \frac{S_{\text{ensemble}}}{A} = S_{\text{system}} = -k \sum_j p_j \ln p_j \]

Plug in our familiar Boltzmann factor?: \( p_j = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} = \frac{e^{-\beta E_j}}{Q} \)

\[ \ln p_j = -\beta E_j - \ln Q \]

\[ S = -k \left( -\beta \sum_j p_j E_j - \sum_j p_j \ln Q \right) \quad \text{but} \sum_j p_j = 1 \quad \text{and} \sum_j p_j E_j = \langle E \rangle \]

\[ S = k\beta E + k \ln Q \quad \text{since} \ \beta = 1/kT \]

\[ S = \frac{E}{T} + k \ln Q \quad \text{or} \]

\[ \bar{S} = \frac{U}{T} + R \ln Q \]
Recall our connection for $U$ to $Q$?

$$U = -\frac{\partial \ln Q}{\partial \beta} = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)$$

So then

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

All right, this is important. It relates entropy back to $Q$. Recall that $Q$ is our connection from microscopic energy levels to macroscopic thermodynamic properties.

Text derives entropy for one particular case: monatomic ideal gas (what contributions to energy do we have? just translation):

$$S = \frac{5}{2} R + R \ln \left( \frac{(2\pi mkT)^{3/2}}{h^3} \frac{V}{N_A} \right)$$

$s$ increases with $T$, $m$, and $V_m$: makes sense!

OK, material for exam ends here. We will forge ahead into chapter 7 to try and cover some of Wednesday’s material now so I can maybe do a little review on Wednesday during lecture.

Clearly to work with entropy we are going to need to be able to calculate changes in entropy as processes occur.

First, let’s deal with constant volume processes.

What do we know about $S$? (think of Carnot and new state variable)

$$dS = \frac{dq_{rev}}{T}$$

So, in a constant volume process, what can we relate $q$ to? Think of 1st law.

$dV = 0$, so $dw = 0$, so $dq = dU$. And what is $dU$? $dU = Cv \, dT$

Ok then $dS = Cv \, dT / T$ and $\Delta S = \int Cv \, \frac{dT}{T}$

If we assume $Cv$ is constant (i.e. monatomic ideal gas) then
\[ \Delta S = C_v \ln \left( \frac{T_f}{T_i} \right) = n \overline{C}_v \ln \left( \frac{T_f}{T_i} \right) \]

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

**What about a constant pressure process?**  \( dq \) is \( dH \), so \( \Delta S = n \overline{C}_p \ln \left( \frac{T_f}{T_i} \right) \)