Week 4

Entropy and the Second Law of Thermodynamics

4.1 Entropy Equations

1/31:
- We define a new state function S by $dS = \delta q_{\text{rev}}/T$ and call it **entropy**.
    - See notes from last time for why this is a state function.
- Verify that the same definition of entropy is a state function for any system.
    - Consider an ideal gas system in thermal equilibrium with an arbitrary system and drive the ideal gas system along a loop.
    - Around the cycle: $\Delta S_{\text{total}} = 0$.
    - Ideal gas:

$$\Delta S_{\text{total}} = \Delta S_1 + \Delta S_2$$
$$= \int \frac{\delta q_{\text{rev}_1}}{T} - \int \frac{\delta q_{\text{rev}_1}}{T}$$
$$= \int \frac{\delta q_{\text{rev}_1}}{T} + \int \frac{\delta q_{\text{rev}_2}}{T}$$

- We must devise a reversible process to calculate the entropy changes for an irreversible process leading to the same final state.
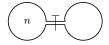
Figure 4.1: Two linked containers.

- Imagine two linked containers, one filled with n moles of gas and the other vacuumed.
- Opening the two containers to each other results in an adiabatic expansion. All vibrational/rotational energy of the molecules is consumed and used for translation.
- Measuring the temperature with spectroscopy (the Maxwell-Boltzmann distribution of each spectral line, plus only the ground rovibrational states are occupied now) shows a drastic drop in temperature.
- We have $\delta q = 0$ and $\delta w = 0$ so that $dU = 0$ and $\Delta T = 0$ overall?
- An isothermal expansion is a reversible process leading to the same final state.

- $dU = 0$ implies $\delta q_{\mathrm{rev}} = -\delta w = P\,dV$.
- We have that

$$\Delta S = \int \frac{\delta q_{\mathrm{rev}}}{T} = \int_{V_0}^{2V_0} \frac{P\,dV}{T} = \int_{V_0}^{2V_0} \frac{nRT}{V}\frac{1}{T}\,dV = nR\ln 2$$

- Using entropy as a state function to predict the vapor pressure in equilibrium with its liquid, from the enthalpy at boiling and the boiling temperature.

Figure 4.2: Vapor pressure thermodynamic loop.

- Consider the above thermodynamic loop, where T is the temperature of the water and P is the pressure above the water.
- We have that

$$\Delta S_1 = \int_T^{T_b} \frac{C_{P_l}}{T}\,dT \qquad \Delta S_2 = \frac{\Delta H_{\mathrm{vap}}}{T_b} \qquad \Delta S_3 = nR\ln\frac{P_0}{P} \qquad \Delta S_4 = \int_{T_b}^T \frac{C_{P_g}}{T}\,dT$$

and that

$$\Delta S_0 = \frac{\Delta H_{\mathrm{vap}}}{T}$$

- We know that ΔS around the loop is zero since S is a state function. We neglect the heat capacity effect. Thus,

$$\frac{\Delta H_{\mathrm{vap}}}{T_b} + nR\ln\frac{P_0}{P} - \frac{\Delta H_{\mathrm{vap}}}{T} = 0$$

$$\ln\frac{P_0}{P} = \frac{\Delta H_{\mathrm{vap}}}{nR}\left(\frac{1}{T} - \frac{1}{T_b}\right)$$

$$P = P_0 e^{-\Delta H_{\mathrm{vap}}/nR(1/T - 1/T_b)}$$

- The above equation gives the vapor pressure at T in terms of the vapor pressure P_0 at T_b.

- **Trouton's rule**: The statement that

$$\frac{\Delta H_{\mathrm{vap}}}{T_b} \approx 85 \pm 5\,\mathrm{J\,mol^{-1}\,K^{-1}}$$

- Discovered this rule as an undergrad after an afternoon's manipulation of data from a book of tables.
- This rule reflects the fact that

$$\frac{\Delta H_{\mathrm{vap}}}{T_b} = \Delta S_{\mathrm{vap}}$$

and implies that ΔS_{vap} is approximately a constant.

- Example of entropy change: The direction of heat flow between two systems (1 and 2) only in thermal contact.

– We have

$$\delta q_{\mathrm{rev}_1} = \delta q_{\mathrm{rev}_2}$$
$$C_{V_1} \, \mathrm{d}T_1 = -C_{V_2} \, \mathrm{d}T_2$$

– Thus,

$$\mathrm{d}S = \mathrm{d}S_1 + \mathrm{d}S_2$$
$$= \frac{\delta q_{\mathrm{rev}_1}}{T_1} + \frac{\delta q_{\mathrm{rev}_2}}{T_2}$$
$$= \frac{C_V \, \mathrm{d}T_1}{T_1} - \frac{C_V \, \mathrm{d}T_1}{T_2}$$
$$= C_V \, \mathrm{d}T_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

– The conclusion is that if $\mathrm{d}T_1 > 0$, then $\mathrm{d}S > 0$. This is the spontaneous direction, the direction that nature chooses, the one in which entropy increases.
– The maximum of S is the equilibrium temperature between the two systems.

• Entropy change of the isothermal mixing of two ideal gases at the same temperature.

– Consider the same two-container setup from Figure 4.1.
– We have that

$$\Delta S = R n_1 \ln \frac{V_1 + V_2}{V_1} + R n_2 \ln \frac{V_1 + V_2}{V_2}$$
$$= R(n_1 + n_2) \left(\frac{n_1}{n_1 + n_2} \ln \frac{V_1 + V_2}{V_1} + \frac{n_2}{n_1 + n_2} \ln \frac{V_1 + V_2}{V_2} \right)$$
$$= R(n_1 + n_2)(-y_1 \ln y_1 - y_2 \ln y_2)$$
$$= R(n_1 + n_2)[-y_1 \ln y_1 - (1 - y_1) \ln(1 - y_1)]$$

■ Note that $y_1 = n_1/(n_1 + n_2) = V_1/(V_1 + V_2)$ is the mole fraction, and similarly for y_2.
– The conclusion is that $\Delta S > 0$.
– The maximum of ΔS is at $y_1 = y_2 = 1/2$.

• **Gibb's paradox**: Suppose you have the same gas on both sides of the containers. Then $\Delta S = nR \ln 2$ for an indistinguishable gas.

– This is wrong.
– Resolved by knowing that the gases *must* be distinguishable.

4.2 Statistical Entropy in Various Systems

• For an isolated system, energy is conserved but the entropy keeps on increasing until the system reaches thermal equilibrium.

• Thermal equilibrium is reached when entropy is maximum for a constant energy.

• The sign of the entropy change in a spontaneous process for an isolated system is positive.

• Entropy is the only macroscopic physical quantity that requires a particular direction for time, sometimes called an **arrow of time**.

• **Second law of thermodynamics**: The entropy of an isolated system can only increase.

- **Clasuius inequality**: The following inequality, where equality holds iff the process is reversible.

$$\Delta S \geq \int \frac{\delta q}{T}$$

  - Considers the isolated system to justify.

- Statistical entropy: $S = k_B \ln W$ where W is the number of microstates of the system (i.e., the number of possible ways the system can be arranged).

  - Shows additivity of the log.
  - When doubling the volume available to a gas, $\Delta S = N k_B \ln 2$. $W_{\text{after}} = 2^N W_{\text{before}}$.
  - The statistical definition of entropy avoids the Gibbs paradox since at a molecular level, we can differentiate between particles.

- Goes over calculating $W(n_1, n_2)$.

- The ways we can distinguish the number of molecules in the container becomes smaller and smaller as we increase the number of particles.

- Consider two identical containers at fixed temperature with N non-interacting indistinguishable molecules $n_1 + n_2 = N$.

  - $W(n_1) = W(n_1, n_2)$ is the number of ways to arrange the molecules between containers 1 and 2.
  - We have

$$\begin{aligned}
\ln W(n_1, n_2) &= \ln N! - \ln n_1! - \ln(N - n_1)! \\
&= N \ln N - N - [n_1 \ln n_1 - n_1 + (N - n_1) \ln(N - n_1) - (N - n_1)] \\
&= N \ln N - n_1 \ln n_1 - (N - n_1) \ln(N - n_1) \\
&= (n_1 + n_2) \ln N - n_1 \ln n_1 - n_2 \ln n_2 \\
&= -n_1 \ln \frac{n_1}{N} - n_2 \ln \frac{n_2}{N} \\
&= N \left(-\frac{n_1}{N} \ln \frac{n_1}{N} - \frac{n_2}{N} \ln \frac{n_2}{N} \right)
\end{aligned}$$

  - Therefore,

$$S = N k_B (-p_1 \ln p_1 - p_2 \ln p_2)$$

- Entropy for a set of systems expressed in terms of the probability for these systems to be in a certain state.

  - Covers $W(n_1, \ldots, n_r)$.
  - We have

$$\begin{aligned}
\ln W &= \ln A! - \sum_i \ln a_i! \\
&= A \ln A - A - \sum_i (a_i \ln a_i - a_I) \\
&= A \ln A - \sum_i a_i \ln a_i \\
&= \left(\sum_i a_i \right) \ln A - \sum_i a_i \ln a_i \\
&= \sum_i \left(-a_i \ln \frac{a_i}{A} \right) \\
&= A \sum_i \left(-\frac{a_i}{A} \ln \frac{a_i}{A} \right) \\
&= A \sum_i (-p_i \ln p_i)
\end{aligned}$$

– Therefore,

$$S = Ak_B \sum_i (-p_i \ln p_i)$$

– We will use this result to derive the Boltzmann Factor.

4.3 MathChapter J: The Binomial Distribution and Stirling's Approximation

From McQuarrie and Simon (1997).

- Counting the number of ways to arrange N distinguishable objects into two groups of size N_1, N_2 where $N_1 + N_2 = N$.

  – There are $N!$ ways to arrange N distinguishable objects, $N!/(N-N_1)!$ ways to arrange the objects in group 1, and $N_2!$ ways to arrange the objects in group 2. Thus, there are

  $$\frac{N!}{(N-N_1)!} \cdot N_2!$$

  permutations of the N objects in two groups.

    ∎ For example, $N = 4$, $N_1 = 3$, and $N_2 = 1$, we are currently counting both $abc : d$ and $bac : d$ as different ways of arranging the four objects into two groups, when clearly such ordering does not matter.

  – Dividing the above by the number of ways to arrange N_1 objects in the first group ($N_1!$) and the number of ways to arrange N_2 objects in the second group ($N_2!$) gives the desired result.

  $$W(N_1, N_2) = \frac{N!}{N_1!N_2!}$$

    ∎ Now we have a result that, as per the previous example, allows us to count only $abc : d$, $bcd : a$, $cda : b$, and $dab : c$.

- McQuarrie and Simon (1997) reviews the binomial expansion in light of the above result's status as a binomial coefficient.

- Counting the number of ways to arrange N distinguishable objects into r groups of size $N_1, \ldots, N_r$ where $N_1 + \cdots + N_r = N$.

  $$W(N_1, \ldots, N_r) = \frac{N!}{N_1! \cdots N_r!}$$

- Note that this quantity is called a **multinomial coefficient** because it occurs in the multinomial expansion $(x_1 + \cdots + x_r)^N$.

- **Asymptotic approximation**: An approximation to a function that gets better as the argument of the function increases.

- **Stirling's approximation**: An asymptotic approximation to $\ln N!$. *Given by*

  $$\ln N! = N \ln N - N$$

  – Proof: We have that

  $$\ln N! = \sum_{n=1}^{N} \ln n$$

  – For N large, this sum behaves more and more like the integral $\int_1^n \ln x \, dx$. Thus, we take

  $$\ln N! = \sum_{n=1}^{N} \ln n \approx \int_1^n \ln x \, dx = N \ln N - N$$

– A refinement of the approximation is the following.

$$\ln N! = N \ln N - N + \frac{1}{2} \ln(2\pi N)$$

4.4 Chapter 20: Entropy and the Second Law of Thermodynamics

From McQuarrie and Simon (1997).

2/1:
- The change of energy alone is not sufficient to determine the direction of a spontaneous process.

    – Although mechanical and chemical systems tend to evolve in such a way as to minimize their energy, we can find examples of spontaneous chemical processes that are not exothermic.
    – Examples include the mixing of two gases and the highly endothermic (and spontaneous) reaction of $Ba(OH)_2$ and NH_4NO_3.
    – Such processes obey the First Law of Thermodynamics, but their spontaneous direction cannot be explained by it.

- Each of these "special cases" involves an increase in the disorder of the system.

    – For example, in the mixing of gases, we can show quantum mechanically that increasing the volume of teh container increases the number of accessible translational states.

- Competition between the drive to lower energy and the drive to increase disorder.

    – Simple mechanical systems can't become that much more disordered; thus, energy considerations dominate.
    – The mixing of gases doesn't change the energy that much; thus, disorder considerations dominate.

- Defining a quantitative state function describing disorder.

    – Note that

$$\delta q_{\text{rev}} = dU - \delta w_{\text{rev}}$$
$$= C_V(T)\, dT + P\, dV$$
$$= C_V(T)\, dT + \frac{nRT}{V}\, dV$$

    is an inexact differential since the second term cannot be written as a derivative of some function of T and V (because T depends on V). In particular, the integral depends on what path through T and V we take.
    – However, if we divide both sides of the above by T, we get an exact differential, i.e., a state function.
    – Note that we can show that this result holds for all systems, not just an ideal gas.

- **Entropy**: The state function describing the disorder of a system. *Denoted by $\boldsymbol{S}$. Given by*

$$dS = \frac{\delta q_{\text{rev}}}{T}$$

- **Integrating factor**: A term that converts an inexact differential to an exact (integrable) differential.

    – $1/T$ is an integrating factor of δq_{rev}.

- Since entropy is a state function, $\Delta S = 0$ for a cyclic process, i.e.,

$$\oint dS = 0$$

- McQuarrie and Simon (1997) calculates ΔS for a process that proceeds from state 1 to state 2 isothermally, and adiabatically/isochorically, to show that the quantity is the same in both cases.

- Justifying $dS = \delta q_{rev}/T$ qualitatively:

  - Increase in heat means increase in disorder (check).
  - Same increase in heat at a lower temperature increases disorder more since there is more order at lower temperatures (check).

- **Isolated** (system): A system that is separated from its surroundings by rigid walls that do not allow matter or energy to pass through them.

- Unlike energy, entropy is not necessarily conserved; it can increase within an isolated system if a spontaneous process takes place therein.

- The entropy of a system is at its maximum when the system is equilibrium; at this point, $dS = 0$.

- Consider an isolated system consisting of two compartments. One compartment holds large, one-component system A, and other holds B. They are separated by a heat-conducting wall.

  - Because of isolation,

$$U_A + U_B = \text{constant} \qquad V_A = \text{constant} \qquad S = S_A + S_B$$
$$V_B = \text{constant}$$

  - Since V_A, V_B are fixed, $dV = 0$, meaning that $dU = \delta q_{rev} + 0$. It follows that

$$dS = dS_A + dS_B$$
$$= \frac{dU_A}{T_A} + \frac{dU_B}{T_B}$$
$$= dU_B \left(\frac{1}{T_B} - \frac{1}{T_A} \right)$$

  - Since the gases A and B can still mix without absorbing energy, we define dS_{prod} as the entropy produced by the system and redefine $\delta q/T$ as dS_{exch} (the entropy exchanged with the surroundings via a transfer of heat).

  - It follows that for an reversible process ($dS_{prod} = 0$), we have

$$dS = \frac{\delta q_{rev}}{T}$$

    while for an irreversible process ($dS_{prod} > 0$), we have

$$dS = dS_{prod} + \frac{\delta q_{irr}}{T} > \frac{\delta q_{irr}}{T}$$

- **Inequality of Clausius**: The following inequality. *Given by*

$$\Delta S \geq \int \frac{\delta q}{T}$$

- **Second Law of Thermodynamics**: There is a thermodynamic state function of a system called the entropy S such that for any change in the thermodynamic state of the system, $dS \geq \delta q/T$, where equality holds iff the change is carried out reversibly.

- "Because the universe itself may be considered to be an isolated system and all naturally occurring processes are irreversible, one statement of the Second Law of Thermodynamics says that the entropy of the universe is constantly increasing. In fact, Clausius summarized the first two laws of thermodynamics by, 'The energy of the Universe is constant; the entropy is tending to a maximum'" (McQuarrie & Simon, 1997, p. 829).

- Relating entropy, a thermodynamic quantity, to a statistical quantity.

  - Consider an ensemble of $\mathcal{A}$ isolated systems, each with number of particles N, volume V, and energy $E(N, V)$.
  - Let $\Omega(E)$ be the degeneracy of E, i.e., the number of quantum states with energy E[1]. Label the $\Omega(E)$ quantum states by $j = 1, 2, \ldots, \Omega(E)$.
  - Let a_j be the number of systems in state j.
  - It follows that the number of ways of having a_1 systems in state 1, a_2 systems in state 2, etc. is given by
  $$W(a_1, \ldots, a_{\Omega(E)}) = \frac{\mathcal{A}!}{a_1! \cdots a_{\Omega(E)}!} = \frac{\mathcal{A}!}{\prod_j (a_j!)}$$

  with $\sum_j a_j = \mathcal{A}$.
  - If every system is in one totally ordered state (i.e., $a_j = \mathcal{A}$ for some j), $W = 1$. On the other end of the spectrum, W can be massive for disorder.
  - As W is a measure of entropy, we are now free to relate S and W, in particular via
  $$S = k_B \ln W$$

    - We choose a log because we want to be able to split S into $S_A + S_B$ and have the math reflect that. In particular, for two systems A, B, $W_{AB} = W_A W_B$, which nicely works out such that
    $$S_{AB} = k_B \ln W_{AB} = k_B \ln W_A + k_B \ln W_B = S_A + S_B$$

  - McQuarrie and Simon (1997) goes over an alternate "derivation" of the above in terms of the degeneracy to get $S = k_B \ln \Omega$.

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[1]Note that for systems relatively far from the ground state, $\Omega(E) \approx e^N$.