# 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.
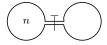


Figure 4.1: Two linked containers.

- 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 $\delta q_{\text{rev}} = -\delta w = P \, dV$.
- We have that

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

- 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

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

and that

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

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

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

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

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

- 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

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

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

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

and implies that $\Delta S_{\text{vap}}$ 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

$$\Delta S = Rn_1 \ln\frac{V_1 + V_2}{V_1} + Rn_2 \ln\frac{V_1 + V_2}{V_2}$$
$$= R(n_1 + n_2)\left(\frac{n_1}{n_1 + n_2}\ln\frac{V_1 + V_2}{V_1} + \frac{n_2}{n_1 + n_2}\ln\frac{V_1 + V_2}{V_2}\right)$$
$$= R(n_1 + n_2)(-y_1 \ln y_1 - y_2 \ln y_2)$$
$$= R(n_1 + n_2)[-y_1 \ln y_1 - (1 - y_1)\ln(1 - y_1)]$$

    - 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 $\Delta S$ 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

2/2:
- 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,

$$S = Ak_{\mathrm{B}} \sum_i (-p_i \ln p_i)$$

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

## 4.3 Further Entropy Relations and Phenomena

2/4: • Verifying that the entropy is at a maximum when all the states have equal probability.

– In the case of just two states,

$$\begin{aligned}
S &= Nk_{\mathrm{B}}(-p_1 \ln p_1 - p_2 \ln p_2) \\
\mathrm{d}S &= Nk_{\mathrm{B}}[-\,\mathrm{d}(p_1 \ln p_1) - \mathrm{d}(p_2 \ln p_2)] \\
&= Nk_{\mathrm{B}}[-\,\mathrm{d}p_1 \cdot \ln p_1 - p_1 \cdot \frac{\mathrm{d}p_1}{p_1} - \mathrm{d}p_2 \cdot \ln p_2 - p_2 \cdot \frac{\mathrm{d}p_2}{p_2}] \\
&= Nk_{\mathrm{B}}(-\,\mathrm{d}p_1)(\ln p_1 - \ln p_2) \\
&= 0
\end{aligned}$$

if $p_1 = p_2$.

■ Thus, since $\mathrm{d}S/\mathrm{d}p_1 \,|_{p_1=1/2} = 0$, we know that a graph of entropy vs. $p_1$ has a maximum at $p_1 = 1/2$.

– In the case of many buckets,

$$\mathrm{d}S = -Nk_{\mathrm{B}} \sum_i \ln p_i \, \mathrm{d}p_i = 0$$

iff all $p_i$ are the same, because then we could pull out the $\ln p_i$ and take $\sum \mathrm{d}p_i = 0$.

• Fluctuations from the equilibrium state are very unlikely in a macroscopic system. Entropy measures the likelihood.

– At equilibrium, we have a number of configurations $W_{\mathrm{eq}}$. Outside of equilibrium, we have a number of configurations $W$.

– Thus,

$$\Delta S = S - S_{\mathrm{eq}} = k_{\mathrm{B}} \ln \frac{W}{W_{\mathrm{eq}}}$$

$$\frac{W}{W_{\mathrm{eq}}} = \mathrm{e}^{\Delta S/k_{\mathrm{B}}}$$

– For $\Delta S = R = 8.31 \,\mathrm{J\,mol^{-1}\,K^{-1}}$, we have that $W = W_{\mathrm{eq}}\mathrm{e}^{N_{\mathrm{A}}}$, which will never happen?

• Deriving the Boltzmann factor by identifying the thermodynamic and statistical entropies.

– Consider two states $E_1, E_2$. Then $\delta q_{\mathrm{rev}} = (E_1 - E_2)$.

– We have

$$\mathrm{d}S = \frac{\delta q_{\mathrm{rev}}}{T} \qquad\qquad \begin{aligned} \mathrm{d}S &= -k_{\mathrm{B}}N\,\mathrm{d}(p_1 \ln p_1 + p_2 \ln p_2) \\ &= -k_{\mathrm{B}}N(\ln p_1 - \ln p_2)\,\mathrm{d}p_1 \end{aligned}$$

– Setting them equal to each other, we get

$$\frac{\mathrm{d}p_1\,(E_1 - E_2)}{T} = -k_{\mathrm{B}}\ln\frac{p_1}{p_2}\,\mathrm{d}p_1$$

$$\frac{E_1 - E_2}{k_{\mathrm{B}}T} = -\ln\frac{p_1}{p_2}$$

$$\frac{p_1}{p_2} = \mathrm{e}^{-(E_1 - E_2)/k_{\mathrm{B}}T}$$

which is the Boltzmann factor, as desired.

- Expressing the entropy in terms of the partition function.

  – Derives

  $$S = k_{\mathrm{B}}T\frac{\partial\ln Q}{\partial T} + k_{\mathrm{B}}\ln Q$$

  from $S = -Nk_{\mathrm{B}}\sum_i p_i\ln p_i$ as in McQuarrie and Simon (1997).

- Entropy of an ideal monatomic gas.

  – Derives

  $$S = \frac{5}{2}Nk_{\mathrm{B}} + Nk_{\mathrm{B}}\ln\left[\left(\frac{2\pi mk_{\mathrm{B}}T}{h^2}\right)^{3/2}\frac{V}{N}g_{e1}\right]$$

  as in McQuarrie and Simon (1997).

  – Note that

  $$\left(\frac{2\pi mk_{\mathrm{B}}T}{h^2}\right)^{3/2} \approx \left(\frac{1}{\lambda_{dB}}\right)^3$$

  where $\lambda_{dB}$ is the de Broglie wavelength.

- The Carnot engine. The most efficient thermal engine between two temperature reservoirs.

  – Recall that the area inside the cycle on a $P/V$ diagram is the work produced by the cycle.
  – It is adiabatic expansion, isothermal expansion, adiabatic compression, isothermal compression.
  – Does the same efficiency analysis as in McQuarrie and Simon (1997).
  – PGS says it's ok to treat the processes as reversible because they're isothermal by definition.

## 4.4 Office Hours (PGS)

- Week 1, Lecture 3: When we calculate the average kinetic energy to be $3k_{\mathrm{B}}T/2$, what constraints do we have on the system. Is it truly any system that can be described by a partition function? And if so, why does this result differ from the one presented in McQuarrie and Simon (1997) for a diatomic ideal gas?

  – There aren't constraints on the system under study.
  – $PV = \frac{2}{3}\langle KE\rangle$ is true without ideality.
  – $\langle E\rangle = 3k_{\mathrm{B}}T/2$ is only true with a monatomic ideal gas.
  – DOFs contribute to $\langle E\rangle$ (at very high temperatures).
    ■ But in the equation from Chapter 17 for a diatomic, some terms disappear as $T \to \infty$.

- Week 1, Lecture 3: What does calculating the expected energy of a harmonic oscillator have to do with anything? Are you just doing it to show that we can for the quantized system? Also, are we integrating because this is a "continuous" partition function, and if it is a continuous partition function, is it so because the harmonic oscillator can, in theory, assume any bond distance even though its *energies* are quantized?

- Week 1, Lecture 3: How is $k_{\mathrm{B}}T$ the average energy of a classical harmonic oscillator? Is it the sum of the kinetic energy and potential energy, both equal to $k_{\mathrm{B}}T/2$? Is this the virial theorem again?

  - Also a high-temperature limit thing.

- What was Week 1 about? It mostly seemed like a lot of examples to sort of motivate the course.

  - Yes, this was basically just to motivate the course.
  - Take away: $k_{\mathrm{B}}T$ determines the range of energies you'll be in for everything.
    - Things much higher in energy won't be **thermally populated**.
    - Things much lower are equally populated.

- Quiz 1, Questions 5-6. Plus will things like surface tension be on the midterm?

  - Surface tension is the same thing as pressure in two dimensions.
  - We can do $\gamma A = nRT$.
  - $A\gamma$ becomes 2 of the kinetic energy $1/2 k_{\mathrm{B}}T$.
    - Work this out for myself!

- Week 2, Lecture 2: The vibrational partition function at $T = h\nu/k_{\mathrm{B}}$ equals zero. What is the significance of this? Is it just that, that the average vibrational energy is equal to zero here?

- Do the rotational and vibrational temperatures have a nice physical interpretation?

  - They are the energies of vibrations/rotations on a scale of temperature instead of energy (the two are directly proportional).
  - The theoretical rotational/vibrational temperature/energy.
    - It's the same temperature as the speeds. When molecules collide, they exchange energy.
    - After enough collisions (as a system tends toward thermal equilibrium), the rotational temperature becomes the same as vibrational.

- Week 3, Lecture 1: In your derivation of the Maxwell-Boltzmann distribution, where does the $4\pi v^2$ come from? Is the sphere you referred to in class the same one as in the textbook, this "velocity space?" If so, could you explain a bit more what a velocity space is?

- The internal energy of a system is only a function of temperature because in the expression for $\langle E \rangle$ in terms of $Q$, $T$ is the only variable that is algebraically in the equation and the partial derivative is held constant with respect to all variables except $T$.

- I'm very confused on the distinction between a reversible and irreversible process.

  - Reversible means that at every point, you are in thermal equilibrium, so you can specify the state of the system.
    - Remember that $T$ is not always specified for a system (only for systems in thermal equilibrium, i.e., that obey the Maxwell-Boltzmann distribution)! The same goes for $P$ and $V$.
  - If the process happens very suddenly or you don't know what the temperature/pressure are during the process, that's irreversible. Something burning in a closed container is irreversible, but at the beginning and end you are in thermal equilibrium, so you can imagine a reversible path between the two.
  - Energy is the same regardless of path, entropy is the same regardless of path.
  - Temperature is not uniform throughout the system during an expansion of a gas from a filled container into a vacuumed container (the system is not in thermal equilibrium). The particles in the filled container will still be at the initial temperature, but those that have left are expending their KE to do so and cooling drastically.

- – *Any* line on a $PV$ diagram describes a reversible process. The processes may differ in terms of non-state functions such as heat exchange or work, but the net $\Delta U$, $\Delta H$, and $\Delta S$ will be the same.
    - ■ The internal energy will be different *along* different paths, but it will make the same net change.
  - – A reversible process need not be isothermal. We can merely consider a piecewise path that contains isothermal components because they are easy to work with mathematically, if the quantity we're interested in calculating is a state function.
  - – If we want to calculate the work for a reversible process, we need $w = -\int_1^2 P\,dV$. If we want to calculate $\Delta U$, we need the state variables $T_1$ and $T_2$ but that's it (since $U$ is a state function of $T$).

- Could you also speak to exact vs. inexact differentials and how to tell if something is a state function by its differential?

  - – If you have a state function, this means that you can express it in terms of the state variables, but you need to know them.
  - – Examples of state variables are energy, temperature, volume, and number of moles.
  - – Once you have a relation between those variables, the state function is uniquely defined between those variables. Entropy is absolute (with physical meaning); enthalpy and energy have defined values once we choose a zero. These latter values, however, have no physical meaning; they only allow us to calculate $\Delta U$ and $\Delta H$, which do have physical meaning.
  - – We find that $\delta q_{\text{rev}} = C_V\,dT$ and $\delta w = -P\,dV$. When we take $\delta q_{\text{rev}} = dU + P\,dV$, this differential does not describe a state function because it is not the derivative of any function ($P$ is a state variable, but it's also a function of $V$ and $T$ [the latter being the problem since it appears in a term with only $dV$]). However, if we divide by $T$ for an ideal gas, then we can get the form $M(T)\,dT + N(V)\,dV$, where $M(T) = C_V(T)/T$ and $N(V) = nR/V$.
    - ■ Note that this differential satisfies $dN/dT = dM/dV = 0$ as per Labalme (2021). In fact, this directly expresses the fact that $M$ is constant with respect to $y$ and $N$ is constant with respect to $x$.
    - ■ Note that according to this definition, we don't theoretically need $M, N$ to only be functions of one variable.
  - – Maxwell's relation: A function $f(x, y)$ such that $df/dx\,dy = df/dy\,dx$.
    - ■ Allows us to relate variables that we might not generally be able to.

- Week 3, Lecture 3: I know you said when you were working with the differential of entropy that $dH = \delta q$ at constant pressure ($dP = 0$). This makes sense. Did you say that at constant volume, we have that $dH = \delta q$ as well?

- Week 3, Lecture 3: How do we obtain the enthalpies of formation at nonstandard temperatures?

- Do we need to know anything about Doppler broadening? I believe you alluded to it once.

- How are $P_{\text{ext}}$ and $P$ related, especially in the context of a $PV$ graph? What exactly is the "$P$" in $w = -\int_1^2 P\,dV$?

  - – In a reversible process, the pressures are the same. This extends to *any* path along a $PV$ diagram, not just an isothermal one, as per our previous discussion.

- What is with the isothermal approximation thing? Do we just approximate everything as isothermal? When can and can't we do this?

- Page 39 of my notes questions.

- What gives us the right to express work during an adiabatic process as an integral with respect to temperature? Is there an equivalent formulation in terms of an integral with respect to $V$?

- Quiz 2, Question 4.

- Week 4, Lecture 1: You calculated that $\Delta S = nR \ln 2$ for $n$ moles of a gas expanding to twice it's initial volume. I assume this doesn't relate to the Gibbs Paradox?

  - The Gibbs paradox says that the final and initial states of two gases mixing are the same, and thus there is no change in entropy.
  - However, we are implicitly assuming that the gases are expanding by virtue of the fact that they're initially separated and thus distinguishable.
  - A paradox doesn't mean that something isn't true, it just means that our understanding is incomplete.
  - The $nR \ln 2$ isn't characteristic of the Gibbs paradox; it's characteristic of a doubling in volume, in whatever context.

- Week 4, Lecture 3: How do you get to $W = W_{\text{eq}} e^{-\Delta S/T}$?

  - It is $+\Delta S$; it's just that $\Delta S$ is a negative quantity when you're moving away from equilibrium.

- In an irreversible process vs. a reversible process, is there a difference in entropy?

  - See the Clausius inequality. If you want more heat, do reversible. If you want more work, do irreversible.

- The experiment in Homework 2, Question 1.

  - The Clément-Desormes experiment.

- Do we need another variable for HW2, Q2?

  - You do need an initial temperature $T_h$.
  - PGS will send a note.

## 4.5 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.
  $$\ln N! = N \ln N - N + \frac{1}{2} \ln(2\pi N)$$

## 4.6   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 the 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

  $$\begin{aligned} \delta q_{\text{rev}} &= \mathrm{d}U - \delta w_{\text{rev}} \\ &= C_V(T)\,\mathrm{d}T + P\,\mathrm{d}V \\ &= C_V(T)\,\mathrm{d}T + \frac{nRT}{V}\,\mathrm{d}V \end{aligned}$$

    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* $S$. *Given by*

  $$\mathrm{d}S = \frac{\delta q_{\text{rev}}}{T}$$

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

  - $1/T$ is an integrating factor of $\delta q_{\text{rev}}$.

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

  $$\oint \mathrm{d}S = 0$$

- McQuarrie and Simon (1997) calculates $\Delta S$ 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 $\mathrm{d}S = \delta q_{\text{rev}}/T$ 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, $\mathrm{d}S = 0$.

- 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 $dU = \delta q_{\text{rev}} + 0$. 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 $dS_{\text{prod}}$ as the entropy produced by the system and redefine $\delta q /T$ as $dS_{\text{exch}}$ (the entropy exchanged with the surroundings via a transfer of heat).

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

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

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

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

- **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

$$S = k_{\text{B}} \ln W$$

---

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

- 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

$$S_{AB} = k_\text{B} \ln W_{AB} = k_\text{B} \ln W_A + k_\text{B} \ln W_B = S_A + S_B$$

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

2/3:
- Since entropy is a state function, we calculate entropy changes via a reversible process.

   - Imagine a gas expanding from $V_1$ to $V_2$ in a non-isolated system.
   - Although this is an adiabatic process, since entropy is a state function, we may perform the easier isothermal calculation for the "equivalent" reversible process.

$$\Delta S_\text{sys} = \int_1^2 \frac{\delta q_\text{rev}}{T} = -\int_1^2 \frac{\delta w_\text{rev}}{T} = \int_{V_1}^{V_2} \frac{P}{T}\,\mathrm{d}V = nR \int_{V_1}^{V_2} \frac{\mathrm{d}V}{V} = nR \ln \frac{V_2}{V_1}$$

   - Note that it is the change to an isothermal integral that allows us to assume $\mathrm{d}U = 0$ (internal energy is a function of only temperature).
   - However, there is still a difference between reversible and irreversible processes.
      - In the reversible, isothermal process, $q_\text{rev} = -w_\text{rev} = -nRT \ln(V_2/V_1)$. Thus,

$$\Delta S_\text{univ} = \Delta S_\text{sys} + \Delta S_\text{surr} = nR \ln \frac{V_2}{V_1} - nR \ln \frac{V_2}{V_1} = 0$$

      as we would expect for an reversible process.
      - In the irreversible, adiabatic process, however, $\Delta S_\text{surr} = 0^{[2]}$. Thus,

$$\Delta S_\text{univ} = nR \ln \frac{V_2}{V_1} > 0$$

      as we would expect for an irreversible process.

- The isothermal mixing of two ideal gases (say $N_2$ and $Br_2$).

   - Because the two gases are ideal, they act independently of each other. Thus,

$$\Delta S_{N_2} = n_{N_2} R \ln \frac{V_{N_2} + V_{Br_2}}{V_{N_2}} \qquad\qquad \Delta S_{Br_2} = n_{Br_2} R \ln \frac{V_{N_2} + V_{Br_2}}{V_{Br_2}}$$

   - It follows that

$$\begin{aligned}
\Delta S &= \Delta S_{N_2} + \Delta S_{Br_2} \\
&= -n_{N_2} R \ln \frac{V_{N_2}}{V_{N_2} + V_{Br_2}} - n_{Br_2} R \ln \frac{V_{Br_2}}{V_{N_2} + V_{Br_2}} \\
&= -n_{N_2} R \ln \frac{n_{N_2}}{n_{N_2} + n_{Br_2}} - n_{Br_2} R \ln \frac{n_{Br_2}}{n_{N_2} + n_{Br_2}} \\
\Delta \overline{S} &= -\frac{n_{N_2}}{n_{N_2} + n_{Br_2}} R \ln \frac{n_{N_2}}{n_{N_2} + n_{Br_2}} - \frac{n_{Br_2}}{n_{N_2} + n_{Br_2}} R \ln \frac{n_{Br_2}}{n_{N_2} + n_{Br_2}} \\
\frac{\Delta_\text{mix}\overline{S}}{R} &= -y_{N_2} \ln y_{N_2} - y_{Br_2} \ln y_{Br_2}
\end{aligned}$$

   where $V \propto n$ by the ideal gas law, $\Delta \overline{S}$ is the *molar* change in entropy, and $y_{N_2}$ is the mole fraction of $N_2$ (same for bromine), and $\Delta_\text{mix}\overline{S}$ indicates that this is the molar change in entropy for the *mixing* of two gases.

---

[2] McQuarrie and Simon (1997) justify $\Delta S_\text{surr} = 0$ for an irreversible *isothermal* process by $\Delta U = 0$ and $P_\text{ext} = 0$ imply $w_\text{irr} = 0$ and therefore $q_\text{irr} = 0$.

– For the isothermal mixing of $N$ ideal gases, we have

$$\Delta_{\text{mix}}\overline{S} = -R\sum_{j=1}^{N} y_j \ln y_j$$

- $\Delta S$ when two equal sized pieces of the same metal at different temperatures $(T_h, T_c)$ are brought into thermal contact and then isolated from the surroundings.

   – Both pieces of metal will approach the same final temperature $T$ as per

$$C_V(T_h - T) = C_V(T - T_c)$$
$$T = \frac{T_h + T_c}{2}$$

   – There is essentially no work done, so $\mathrm{d}U = \delta q_{\text{rev}}$.
   – Thus, taking $C_V$ to be constant from $T_c$ to $T_h$ yields

$$\Delta S = \int_{T_1}^{T_2} \frac{\delta q_{\text{rev}}}{T} = \int_{T_1}^{T_2} \frac{C_V\,\mathrm{d}T}{T} = C_V \ln \frac{T_2}{T_1}$$

   – Therefore, we have

$$\Delta S_h = C_V \ln \frac{T_h + T_c}{2T_h} \qquad\qquad \Delta S_c = C_V \ln \frac{T_h + T_c}{2T_c}$$

   – It follows that

$$\Delta S = \Delta S_h + \Delta S_c = C_V \ln \frac{(T_h + T_c)^2}{4T_h T_c}$$

   where

$$(T_h - T_c)^2 = T_h^2 - 2T_h T_c + T_c^2 > 0$$
$$T_h^2 + 2T_h T_c + T_c^2 = (T_h + T_c)^2 > 4T_h T_c$$

   implies that $\Delta S > 0$, as desired for an irreversible process.

- The Carnot cycle (for a steam engine).

   – Each cycle, the engine (system) "withdraws energy $[q_h]$ as heat from some high-temperature thermal reservoir, uses some of the energy to do work $[w]$, and then discharges the rest of the energy $[q_c]$ as heat to a lower-temperature thermal reservoir" (McQuarrie & Simon, 1997, p. 838).
   – Treating the process as reversible (since both internal energy and entropy as state functions) gives us the following analysis.
   – Since this is a cycle, we have that

$$\Delta U_{\text{engine}} = w + q_{\text{rev,h}} + q_{\text{rev,c}} = 0 \qquad\qquad \Delta S_{\text{engine}} = \frac{\delta q_{\text{rev,h}}}{T_h} + \frac{\delta q_{\text{rev,c}}}{T_c}$$

   – It follows if we define the maximum efficiency of the engine to be the quotient of work done by the engine $(-w)$ and heat input $(q_{\text{rev,h}})$ that

$$\text{maximum efficiency} = \frac{-w}{q_{\text{rev,h}}}$$
$$= \frac{q_{\text{rev,h}} + q_{\text{rev,c}}}{q_{\text{rev,h}}}$$
$$= 1 + \frac{-T_c q_{\text{rev,h}}/T_h}{q_{\text{rev,h}}}$$
$$= \frac{T_h - T_c}{T_h}$$

- It follows for typical values of $T_h = 573\,\mathrm{K}$ and $T_c = 373\,\mathrm{K}$ that maximum efficiency $\approx 35\%$.
  - Moreover, it implies that engines run with higher-temperature heat reservoirs and lower-temperature cold reservoirs are more efficient, regardless of design.
  - Note that $T_h = T_c$ implies that maximum efficiency $= 0\%$, i.e., no net work can be obtained from an isothermal cyclic process.

- The above result leads to **Kelvin's statement of the Second Law**.

- **Kelvin's statement of the Second Law**: A closed system operating in an isothermal cyclic manner cannot convert heat into work without some accompanying change in the surroundings.

- Expressing entropy in terms of a partition function.

$$
\begin{aligned}
S_{\mathrm{ensemble}} &= k_{\mathrm{B}} \ln W \\
&= k_{\mathrm{B}} \ln \frac{\mathcal{A}!}{\prod_j a_j!} \\
&= k_{\mathrm{B}} \ln \mathcal{A}! - k_{\mathrm{B}} \sum_j \ln a_j! \\
&= k_{\mathrm{B}} \mathcal{A} \ln \mathcal{A} - k_{\mathrm{B}} \mathcal{A} - k_{\mathrm{B}} \sum_j a_j \ln a_j + k_{\mathrm{B}} \sum_j a_j && \text{(Stirling's approximation)} \\
&= k_{\mathrm{B}} \mathcal{A} \ln \mathcal{A} - k_{\mathrm{B}} \sum_j a_j \ln a_j && \left(\textstyle\sum_j a_j = \mathcal{A}\right) \\
&= k_{\mathrm{B}} \mathcal{A} \ln \mathcal{A} - k_{\mathrm{B}} \sum_j p_j \mathcal{A} \ln p_j \mathcal{A} && \left(p_j = a_j / \mathcal{A}\right) \\
&= k_{\mathrm{B}} \mathcal{A} \ln \mathcal{A} - k_{\mathrm{B}} \mathcal{A} \sum_j p_j \ln p_j - k_{\mathrm{B}} \mathcal{A} \ln \mathcal{A} \sum_j p_j \\
\frac{S_{\mathrm{ensemble}}}{\mathcal{A}} &= -k_{\mathrm{B}} \sum_j p_j \ln p_j && \left(\textstyle\sum_j p_j = 1\right) \\
S_{\mathrm{system}} &= -k_{\mathrm{B}} \sum_j p_j \ln p_j \\
&= -k_{\mathrm{B}} \sum_j \frac{\mathrm{e}^{-\beta E_j}}{Q} \left(-\beta E_j - \ln Q\right) \\
&= \beta k_{\mathrm{B}} \sum_j \frac{E_j \mathrm{e}^{-\beta E_j}}{Q} + k_{\mathrm{B}} \ln Q \sum_j \frac{\mathrm{e}^{-\beta E_j}}{Q} \\
&= \frac{1}{T} \cdot \langle E \rangle + k_{\mathrm{B}} \ln Q \\
S_{\mathrm{system}} &= k_{\mathrm{B}} T \frac{\partial \ln Q}{\partial T} + k_{\mathrm{B}} \ln Q
\end{aligned}
$$

- For a monatomic ideal gas where all atoms are in their ground electronic state, we have

$$
\overline{S} = \frac{5}{2} R + R \ln \left[ \left( \frac{2\pi m k_{\mathrm{B}} T}{h^2} \right)^{3/2} \frac{\overline{V} g_{e1}}{N_{\mathrm{A}}} \right]
$$

- The mixing of two ideal gases (say $N_2$ and $Br_2$) from a molecular perspective.

  - Since the natural log in $\overline{S}$ for a monatomic ideal gas contains the same number of terms involving $V$ as for a diatomic ideal gas, we have that

$$
\begin{aligned}
S &= N k_{\mathrm{B}} \ln V + \text{terms not involving } V \\
&= nR \ln V + \text{terms not involving } V
\end{aligned}
$$

for both $N_2$ and $Br_2$.

– Thus, the initial state is given by

$$
\begin{aligned}
S_1 &= S_{1,N_2} + S_{1,Br_2} \\
&= n_{N_2} R \ln V_{N_2} + n_{Br_2} R \ln V_{Br_2} + \text{terms not involving } V
\end{aligned}
$$

and the final state is given by

$$
\begin{aligned}
S_2 &= S_{2,N_2} + S_{2,Br_2} \\
&= n_{N_2} R \ln(V_{N_2} + V_{Br_2}) + n_{Br_2} R \ln(V_{N_2} + V_{Br_2}) + \text{terms not involving } V
\end{aligned}
$$

– Therefore,

$$
\begin{aligned}
\Delta_{\text{mix}} S &= S_2 - S_1 \\
&= n_{N_2} R \ln \frac{V_{N_2} + V_{Br_2}}{V_{N_2}} + n_{Br_2} R \ln \frac{V_{N_2} + V_{Br_2}}{V_{Br_2}} \\
\frac{\Delta_{\text{mix}} \overline{S}}{R} &= -y_{N_2} \ln y_{N_2} - y_{Br_2} \ln y_{Br_2}
\end{aligned}
$$

as expected.

• Relating $S = k_B \ln W$ to $dS = \delta q_{\text{rev}}/T$ (and proving that $\beta = 1/k_B T$!).

– We have that

$$
\begin{aligned}
S &= -k_B \sum_j p_j \ln p_j \\
\frac{dS}{dp_j} &= -k_B \sum_j \left( p_j \cdot \frac{1}{p_j} + 1 \cdot \ln p_j \right) \\
dS &= -k_B \sum_j (dp_j + \ln p_j \, dp_j) \\
&= -k_B \sum_j (-\beta E_j - \ln Q) \, dp_j \\
&= \beta k_B \sum_j E_j \, dp_j + \ln Q \sum_j dp_j \\
&= \beta k_B \, \delta q_{\text{rev}} \qquad\qquad (\textstyle\sum_j p_j = 1 \Rightarrow \sum dp_j = 0)
\end{aligned}
$$

as desired.

– Additionally, the above result implies that $\beta k_B$ is an integrating factor of $\delta q_{\text{rev}}$, i.e.,

$$
\begin{aligned}
\beta k_B &= \frac{1}{T} \\
\beta &= \frac{1}{k_B T}
\end{aligned}
$$