Week 4

Entropy and the Second Law of Thermodynamics

4.1 Entropy Equations

- 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.
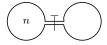

Figure 4.1: Two linked containers.

- 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 ΔS 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 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

$$\delta q_{\text{rev}_1} = \delta q_{\text{rev}_2}$$
$$C_{V_1} \, dT_1 = -C_{V_2} \, dT_2$$

  - Thus,

$$dS = dS_1 + dS_2$$
$$= \frac{\delta q_{\text{rev}_1}}{T_1} + \frac{\delta q_{\text{rev}_2}}{T_2}$$
$$= \frac{C_V \, dT_1}{T_1} - \frac{C_V \, dT_1}{T_2}$$
$$= C_V \, dT_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

  - The conclusion is that if $dT_1 > 0$, then $dS > 0$. 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 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 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,

$$S = Nk_B(-p_1 \ln p_1 - p_2 \ln p_2)$$
$$dS = Nk_B[-d(p_1 \ln p_1) - d(p_2 \ln p_2)]$$
$$= Nk_B[-dp_1 \cdot \ln p_1 - p_1 \cdot \frac{dp_1}{p_1} - dp_2 \cdot \ln p_2 - p_2 \cdot \frac{dp_2}{p_2}]$$
$$= Nk_B(-dp_1)(\ln p_1 - \ln p_2)$$
$$= 0$$

  if $p_1 = p_2$.
  - Thus, since $dS/dp_1\,|_{p_1=1/2} = 0$, we know that a graph of entropy vs. p_1 has a maximum at $p_1 = 1/2$.

  – In the case of many buckets,
$$dS = -Nk_B \sum_i \ln p_i \, dp_i = 0$$

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

- 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_{eq}. Outside of equilibrium, we have a number of configurations W.
  – Thus,

$$\Delta S = S - S_{\mathrm{eq}} = k_B \ln \frac{W}{W_{\mathrm{eq}}}$$
$$\frac{W}{W_{\mathrm{eq}}} = e^{\Delta S/k_B}$$

  – For $\Delta S = R = 8.31 \, \mathrm{J\,mol^{-1}\,K^{-1}}$, we have that $W = W_{\mathrm{eq}} e^{N_A}$, 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

$$dS = \frac{\delta q_{\mathrm{rev}}}{T} \qquad\qquad dS = -k_B N \, d(p_1 \ln p_1 + p_2 \ln p_2)$$
$$= -k_B N (\ln p_1 - \ln p_2) \, dp_1$$

– Setting them equal to each other, we get

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

$$\frac{E_1 - E_2}{k_B T} = -\ln \frac{p_1}{p_2}$$

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

which is the Boltzmann factor, as desired.

- Expressing the entropy in terms of the partition function.

  – Derives

  $$S = k_B T \frac{\partial \ln Q}{\partial T} + k_B \ln Q$$

  from $S = -N k_B \sum_i p_i \ln p_i$ as in McQuarrie and Simon (1997).

- Entropy of an ideal monatomic gas.

  – Derives

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

  as in McQuarrie and Simon (1997).

  – Note that

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

  where λ_{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 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 $N_1, \dots, N_r$ where $N_1 + \cdots + N_r = N$.

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

- 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.

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

4.5 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

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

  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 δq_{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 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 $\mathrm{d}S = \delta q_{\text{rev}}/T$ 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 $dU = \delta q_{rev} + 0$. 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

$$S = k_B \ln W$$

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[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

$$S_{AB} = k_B \ln W_{AB} = k_B \ln W_A + k_B \ln W_B = S_A + S_B$$

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

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.

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

   ■ Note that it is the change to an isothermal integral that allows us to assume $dU = 0$ (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.

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[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

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

- ΔS 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 $T_h = 573\,\text{K}$ and $T_c = 373\,\text{K}$ 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.

$$S_{\text{ensemble}} = k_B \ln W$$

$$= k_B \ln \frac{\mathcal{A}!}{\prod_j a_j!}$$

$$= k_B \ln \mathcal{A}! - k_B \sum_j \ln a_j!$$

$$= k_B \mathcal{A} \ln \mathcal{A} - k_B \mathcal{A} - k_B \sum_j a_j \ln a_j + k_B \sum_j a_j \qquad \text{(Stirling's approximation)}$$

$$= k_B \mathcal{A} \ln \mathcal{A} - k_B \sum_j a_j \ln a_j \qquad \left(\sum_j a_j = \mathcal{A}\right)$$

$$= k_B \mathcal{A} \ln \mathcal{A} - k_B \sum_j p_j \mathcal{A} \ln p_j \mathcal{A} \qquad \left(p_j = a_j / \mathcal{A}\right)$$

$$= k_B \mathcal{A} \ln \mathcal{A} - k_B \mathcal{A} \sum_j p_j \ln p_j - k_B \mathcal{A} \ln \mathcal{A} \sum_j p_j$$

$$\frac{S_{\text{ensemble}}}{\mathcal{A}} = -k_B \sum_j p_j \ln p_j \qquad \left(\sum_j p_j = 1\right)$$

$$S_{\text{system}} = -k_B \sum_j p_j \ln p_j$$

$$= -k_B \sum_j \frac{e^{-\beta E_j}}{Q} (-\beta E_j - \ln Q)$$

$$= \beta k_B \sum_j \frac{E_j e^{-\beta E_j}}{Q} + k_B \ln Q \sum_j \frac{e^{-\beta E_j}}{Q}$$

$$= \frac{1}{T} \cdot \langle E \rangle + k_B \ln Q$$

$$S_{\text{system}} = k_B T \frac{\partial \ln Q}{\partial T} + k_B \ln Q$$

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

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

- 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

$$S = N k_B \ln V + \text{terms not involving } V$$

$$= n R \ln V + \text{terms not involving } V$$

for both N_2 and Br_2.

– Thus, the initial state is given by

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

and the final state is given by

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

– Therefore,

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

as expected.

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

　　– We have that

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

as desired.

　　– Additionally, the above result implies that βk_B is an integrating factor of δq_{rev}, i.e.,

$$\beta k_B = \frac{1}{T}$$
$$\beta = \frac{1}{k_B T}$$

4.6　Chapter 21: Entropy and the Third Law of Thermodynamics

From McQuarrie and Simon (1997).

• In this chapter, we will learn how to calculate absolute (as opposed to relative) values of entropy.

• Relating thermodynamic quantities to entropy.

- It follows from the First Law of Thermodynamics that

$$dU = \underbrace{T\,dS}_{\delta q_{\mathrm{rev}}} \underbrace{-P\,dV}_{\delta w_{\mathrm{rev}}}$$

- We have that the total differential of $U(V,T)$ is

$$dU = \frac{\partial U}{\partial T}\,dT + \frac{\partial U}{\partial V}\,dV$$

- Combining the two above equations, we have that

$$T\,dS - P\,dV = \frac{\partial U}{\partial T}\,dT + \frac{\partial U}{\partial V}\,dV$$

$$dS = \frac{1}{T}\frac{\partial U}{\partial T}\,dT + \frac{1}{T}\left(P + \frac{\partial U}{\partial V}\right)dV$$

$$= \frac{C_V\,dT}{T} + \frac{1}{T}\left(P + \frac{\partial U}{\partial V}\right)dV$$

- It follows by comparing the above with the total differential of $S(V,T)$ that

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \qquad\qquad \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

- Since

$$dH = dU + P\,dV + V\,dP = T\,dS + V\,dP$$

we can proceed in a similar manner to the above to obtain

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \qquad\qquad \left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right) - V\right]$$

- **Third Law of Thermodynamics**: Every substance has a finite positive entropy, but at zero kelvin, the entropy may become zero, and does so in the case of a perfectly crystalline substance.

  - While the first and second laws provide state functions (internal energy and entropy, respectively), the third law provides a numerical scale for entropy.

- The third law, although formulated before quantum mechanics, follows nicely from it: At absolute zero, every system in an ensemble will be in the same energy state, so $W = 1$; it follows that $S = k_B \ln 1 = 0$.

  - If, however, the ground state has a degeneracy of n, then

$$S(0\,\mathrm{K}) = -k_B \sum_j p_j \ln p_j$$

$$= -k_B \sum_{j=1}^{n} \frac{1}{n} \ln \frac{1}{n}$$

$$= k_B \ln n$$

  - Nevertheless, even for a degeneracy of N_A, we will only have $S(0\,\mathrm{K}) \approx 7.56 \times 10^{-22}\,\mathrm{J\,mol^{-1}\,K^{-1}}$, which is far less than any measurable value.

- Because of the third law, we can define entropy absolutely (assuming no phase change between 0 and T).

$$S(T) = S(0) + S(T) - S(0)$$

$$= S(0) + \Delta S$$

$$= S(0) + \int_0^T \frac{C_P(t)}{t}\,dt$$

$$= \int_0^T \frac{C_P(t)}{t}\,dt$$

- Accounting for phase changes.

    - A phase change is a great example of a reversible process since we only need the temperature to be slightly above or slightly below the transition temperature T_{trs} to accomplish it.
    - Thus,

$$\Delta_{\text{trs}}S = \frac{q_{\text{rev}}}{T_{\text{trs}}} = \frac{\Delta_{\text{trs}}H}{T_{\text{trs}}}$$

    - It follows that, as applicable,

$$S(T) = \int_0^{T_{\text{fus}}} \frac{C_P^s(t)}{t}\,\mathrm{d}t + \frac{\Delta_{\text{fus}}H}{T_{\text{fus}}} + \int_{T_{\text{fus}}}^{T_{\text{vap}}} \frac{C_P^l(t)}{t}\,\mathrm{d}t + \frac{\Delta_{\text{vap}}H}{T_{\text{vap}}} + \int_{T_{\text{vap}}}^{T} \frac{C_P^g(t)}{t}\,\mathrm{d}t$$

    - Note that with typical values plugged in, $\Delta_{\text{fus}}S \ll \Delta_{\text{vap}}S$.

- **Debye T^3 law**: As $T \to 0$ (i.e., for about $T = 0 - 15\,\text{K}$), $C_P^s(T) \to T^3$ for most nonmetallic crystals and $C_P^s(T) \to aT + bT^3$ ($a, b \in \mathbb{R}_{\geq 0}$) for most metallic crystals.

    - It follows by the absolute definition of S that

$$S(T) = \frac{C_P(T)}{3}$$

    at low temperatures for nonmetallic solids.

- **Debye temperature**: A constant characteristic of the solid. *Denoted by* $\boldsymbol{\Theta_D}$.

- **Third-law entropy**: An absolute entropy value calculated according to the convention that $S(0\,\text{K}) = 0$. *Also known as* **practical absolute entropy**.

- McQuarrie and Simon (1997) calculates the third-law entropy of N_2 based on various thermodynamic data.

- **Standard entropy**: An entropy value of a gas as presented in the literature. *Denoted by* $\boldsymbol{S^\circ}$.

    - Standard entropies are, by convention, corrected for the nonideality of the gas at one bar (for how to calculate this correction, see Chapter 22).

- McQuarrie and Simon (1997) rederives $S(0\,\text{K}) = k_B \ln n$ from a partition function approach, and then gives a specific example for N_2, noting how well this value correlates with the one from the previous example.

    - "This type of agreement is quite common, and in many cases the statistical thermodynamic value is more accurate than the calorimetric value... The accepted literature values are often a combination of statistical thermodynamic and calorimetric values" (McQuarrie & Simon, 1997, p. 863).
    - Also gives a linear symmetric example (CO_2).

- Entropy trends.

    1. "The standard molar entropies of the gaseous substances are the largest, and the standard molar entropies of the solid substances are the smallest" (McQuarrie & Simon, 1997, p. 865).
    2. "The increase in standard molar entropy of the noble gases is a consequence of their increasing mass as we move down the periodic table" (McQuarrie & Simon, 1997, p. 865).

        - More mass implies more translational energy levels are available implies more disorder.
        - This is a consequence of quantum mechanics — considering the formula for the energy of a particle in a 3D box, note that m is in the denominator. Thus, increasing m means that the levels are more closely spaced, and hence more are readily accessible.

3. "Generally speaking, the more atoms of a given type in a molecule, the greater is the capacity of the molecule to take up energy and thus the greater is its entropy" (McQuarrie & Simon, 1997, p. 866).

   – More atoms implies more vibrational modes implies more disorder.

4. "For molecules with approximately the same molecular masses, the more compact the molecule is, the smaller is its entropy" (McQuarrie & Simon, 1997, p. 867).

   – Between isomers, the one with more unrestricted motion will have greater entropy.

- We can calculate the entropy for substances that "don't exist" via alternate paths.

  – For example, Br_2 is a liquid at $298\,K$, but we can still calculate $S°[Br_{2(g)}]$ by imagining the following path: Raise $Br_{2(l)}$ to its boiling point; vaporize it; cool it back down to $298\,K$.

  – This calculated value is in agreement with the spectroscopic value.

- **Residual entropy**: The difference between the calculated molar entropy of a substance and its experimental molar entropy. *Given by*
$$\overline{S}_{\text{calc}} - \overline{S}_{\text{exp}}$$

  – We define residual entropy this way because wherever there are discrepancies, it so happens that $S_{\text{calc}} > S_{\text{exp}}$.

- Large residual entropies are encountered for the linear molecules CO and N_2O.

  – This is because these molecules have small dipole moments, so upon crystallization, there is not a strong tendency for the molecule to align in the most energetically favorable way.

  – Thus, with molecules already locked in higher energy states at T_{fus}, as we cool to $0\,K$, we do not have a "perfect" crystal.

  – Since the ground state is two-fold degenerate in both of these cases (we have CO and OC, and NNO and ONN), $\overline{S}(0\,K) = R\ln 2$ here.

- We can similarly account for the larger still residual entropy in H_3CD by noting that the ground state is four-fold degenerate, and thus $\overline{S}(0\,K) = R\ln 4$ here.

- We can use standard molar entropies to calculate the entropy changes of chemical reactions.