Thermodynamics Lecture Notes: Chapter 8

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8 Entropy and the second and third law of Thermodynamics

8.1 Reversible and irreversible processes

Consider an isothermal expansion of an n-mol ideal gas at $T = T_0$ changing its state from $A(V_a, P_a, T_0)$ to $B(V_b, P_b, T_0)$ through a quasi-static path (see Chapter 7, and top row of the figure below). This process follows the line given by $PV = nRT_0$ on the V-P plane. Since there is no temperature change, $\Delta E_{int} = 0$ and from the first law of thermodynamics follows $Q = W$, where work W is given by

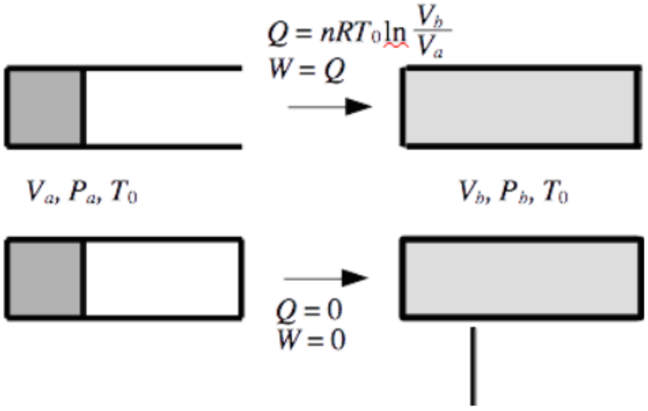
$$W_{A \to B} = \int_A^B P dV = nRT_0 \int_{V_a}^{V_b} \frac{dV}{V} = nRT_0 \ln \frac{V_b}{V_a} \tag{1}$$

thus

$$Q_{A \to B} = nRT_0 \ln \frac{V_b}{V_a} \tag{2}$$

Once the system is at the state B, we can make the system to follow the same path back to A by applying $-Q_{A \to B}$ and , just reversing the sign. Any process that can be reversed by changing the sign of Q and W is called *reversible.*

Now consider a process where a thermally isolated container with a volume V_b is divided into two by a tight thermally isolating wall. One section is filled with an n-mol ideal gas at $A(V_a, P_a, T_0)$ and the other vacuum. Now we remove the wall and let the gas to expand into the whole volume (see bottom row of figure below). Since the container is thermally isolated, Q = 0, and since gas expands without moving anything, W = 0. The first law of thermodynamics leads to $\Delta E_{int} = 0$. The final state is $B(V_b, P_b, T_0)$. Since the internal energy depends only on temperature, no change of temperature in this process. The process cannot be shown as a quasi-static path on the V-P plane. Clearly, this process cannot be reversed by simply changing the sign of Q and W. Any process that cannot be reversed by changing the sign of Q and W is called *irreversible.*



8.2 Entropy

For a **reversible process**, the change of entropy of a thermodynamic system, ΔS, for a change of its state from A to B with heat Q and at a constant temperature T, is given by

$$\Delta S = \frac{Q}{T} \tag{3}$$

where the temperature is in Kelvin. If the temperature of the system is not constant, ΔS is given by

$$\Delta S = \int_A^B dS = \int_A^B \frac{\delta Q}{T} \tag{4}$$

where the integral follows a quasi-static path from A to B. Note that $\frac{Q}{T}$ of infinitesimally small step on the path is given by $\frac{\delta Q}{T}$. It can be shown that ΔS is independent of the path, unlike the heat. Thus, the entropy, S, is a state variable such as volume and temperature and $\Delta S = S(B) - S(A)$.

We demonstrate the fact that ΔS does not depend on the path, by calculating ΔS explicitly for a change of state $A(V_a, P_a, T_0)$ to $B(V_b, P_b, T_0)$ for an n-mol ideal gas in two different reversible paths. As shown above, the state from A to B can be achieved through isothermal expansion, where heat is given by

$$Q = nRT_0 \ln \frac{V_b}{V_a} \tag{5}$$

Since the temperature does not change in the process, the entropy change is then given by

$$\Delta S_{ab} = \frac{Q}{T_0} = nR \ln \frac{V_b}{V_a} \tag{6}$$

As an alternative path, we consider reaching B in two steps, first decreasing the pressure under constant volume to reach $D(V_a, P_b, T_d)$, followed by increasing the volume under constant pressure (see again Chapter 7). For the heat, we have:

$$A \to D : Q_{ad} = nC_V dT \quad \text{and} \quad D \to B : Q_{db} = nC_P dT \tag{7}$$

which leads to

$$\Delta S_{ad} = nC_V \int_{T_0}^{T_d} = nC_V \ln \frac{T_d}{T_0} \quad \text{and} \quad \Delta S_{db} = nC_P \int_{T_d}^{T_0} = n(C_V + R) \ln \frac{T_0}{T_d} \tag{8}$$

The total entropy change is given by

$$\Delta S'_{ab} = \Delta S_{ad} + \Delta S_{db} = nC_V \ln \frac{T_d}{T_0} + n(C_V + R) \ln \frac{T_0}{T_d} = nR \ln \frac{T_0}{T_d} \tag{9}$$

Using the gas low, $PV = nRT$, we obtain,

$$\frac{T_0}{T_d} = \frac{V_b P_b}{V_a P_b} \tag{10}$$

from which follows that

$$\frac{T_0}{T_d} = \frac{V_b}{V_a} \tag{11}$$

showing that the two different paths give same ΔS. Since $V_a < V_b$, we have $\Delta S > 0$.

The considered paths can be indeed reversed, i.e. $C \to A$, by changing the sign of Q and W, with negative entropy ΔS. Therefore, entropy change for a loop such as $A \to B \to C \to A$,

$$\Delta S_{ab} + \Delta S_{bc} + \Delta S_{ca} = \oint \frac{\delta Q}{T} = 0 \tag{12}$$

i.e. it is always 0. We conclude that ΔS does not depend on the path, **thus S is a state variable**.

For **irreversible processes**, it turns out

$$\Delta S = \int_A^B \frac{\delta Q_{reversible}}{T} > \int_A^B \frac{\delta Q_{irreversible}}{T} \tag{13}$$

For the state change of $A(V_a, P_a, T_0)$ to $B(V_b, P_b, T_0)$ discussed above, indeed we have

$$\int_A^B \frac{\delta Q}{T} = nRT_0 \ln \frac{V_b}{V_a} > 0 \quad \text{and} \quad \int_A^B \frac{\delta Q}{T} = 0 \tag{14}$$

Therefore, we can write,

$$\Delta S \geq \int_A^B \frac{\delta Q}{T} \tag{15}$$

where the equal sign holds only for reversible processes, i.e. entropy change is given by

$$\Delta S = \int_A^B \frac{\delta Q}{T} \tag{16}$$

only for the reversible process. If we consider a thermally isolated system, there is no heat exchange for any process, i.e. $\Delta S \geq 0$.

Important, clarifying remarks to original lecture notes (consider slides for more details):

- So far, we have considered the change of entropy due to heat exchange with the environment: $dS_{env} = \frac{\delta Q}{T}$
- The total entropy change of a thermodynamic system is $dS_{system} = dS_{env} + dS_{prod}$.
- With dS_{prod} being the entropy production due to dissipation within the system (not always to compute that).
- For irreversible processes: $\mathrm{dS}_{prod} > 0$.
- For reversible processes, $dS_{env} = \frac{\delta Q}{T}$, but $dS_{prod} = 0 \to dS_{system} = dS_{env} = \frac{dQ}{T}$.
- In general: $dS_{system} \geq dS_{env}$, i.e. $dS_{system} \geq \frac{\delta Q}{T}$, with **equality only for reversible processes!!**

8.3 The second law of thermodynamics

The second law of thermodynamics states: In any thermodynamic process, in which a **thermally isolated system** goes from one state to another state, the entropy cannot be decreased, i.e. $dS_{system} >= 0$.

8.4 The third law of thermodynamics

The third law of thermodynamics states: The entropy of a system converges to a constant value $S_0 = 0$ for $T \to 0$ independent of all the other properties for the particular system.

But S converging against a constant is a rather weak statement, and valid for classical thermodynamics. Instead, in statistical thermodynamics : S converges against $0J/K$ for $T \to 0$.

The third law also requires that the specific heat C_P, C_V converges to 0 for $T \to 0$ (because $dS = \delta Q/T = nCdT/T$).

8.5 Entropy and the first law of thermodynamics

For reversible processes with a fixed temperature T, the heat Q can be obtained from the change of the entropy, ΔS as or **for an infinitesimally small path**, $\delta Q = TdS$. Then, The first law of thermodynamics can be written as

$$dE_{int} = \delta Q - \delta W = TdS - PdV \tag{17}$$

where the terms of the right side consist of state variables, not depending on the path. Therefore, it is valid even for irreversible process. One may summarise as:

- $\delta Q = TdS \to$ Only for reversible case
- $\delta W = PdV \to$ Only for reversible case
- $dE_{int} = \delta Q - \delta W \to$ always valid
- $dE_{int} = TdS - PdV \to$ always valid

For irreversible process, we have $TdS \geq \delta Q$, thus $PdV < \delta W$.

The slides provide many examples of how to apply the first and second law to simple homogenous, inhomogeneous and stationary thermodynamic systems. Consult the slides for more details.

8.6 Statistical interpretation of Entropy

Once we obtain, $dE_{int} = TdS - PdV$, temperature, T, can be given by

$$\frac{1}{T} = \frac{1}{(\partial E_{int}/\partial S)_V} = \left(\frac{\partial S}{\partial E_{int}}\right)_V \tag{18}$$

While deriving the Boltzmann constant in Chapter 5, we obtained the expression:

$$\frac{d \ln \Omega(E)}{E} = \frac{1}{kT} \tag{19}$$

where, k is the Boltzmann constant, and $\Omega(E)$ is the number of states with energy E as an thermal equilibrium condition. This leads to

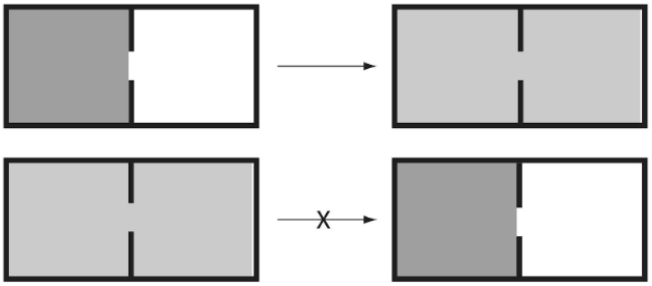
$$k\frac{d\ln\Omega(E_{int})}{dE_{int}} = \left(\frac{\partial S}{\partial E_{int}}\right)_V \tag{20}$$

By integrating the both sides, we get

$$S = k\ln\Omega \tag{21}$$

which is the *definition of entropy in statistical physics*: the entropy of a particular macrostate, S, is given by the formula, $S = k\ln\Omega$, where Ω is the number of microstates associated to the particular macrostate. At $T = 0$, there is only one state. The evolution of a thermodynamic system is in the direction from an "ordered" state to a more "chaotic" state: e.g. vacuum expansion (as the probability for a chaotic is higher than for a more ordered state).

8.6.1 Entropy of free expansion a la statistical mechanics



We will now compute the entropy change for the free expansion process. Let's assume we have a total of N ideal gas molecules placed in a container with volume V_a. In that volume, there are m possible states that the gas molecule can take. The number of possible configuration taken by the N molecules, Ω, is then given by

$$\Omega = \binom{m}{N} = \frac{m!}{N!(m-N)!} \tag{22}$$

and entropy is thus, given by

$$S = k\ln\Omega = k\ln\frac{m!}{N!(m-N)!} \tag{23}$$

Since we are considering a macroscopic system, both m and N are large, where $\ln n! \approx n\ln n - n$ (Sterling's approximation) can be used. This leads to

$$S = k\ln\frac{m!}{N!(m-N)!} \approx k[m\ln m - N\ln N - (m-N)\ln(m-N)] \tag{24}$$

Since we are considering an ideal gas, the gas density must be very small, thus we have $m \gg N$, and the following approximation holds:

$$\begin{aligned} m\ln m - N\ln N - (m-N)\ln(m-N) &= m\ln\frac{m}{m-N} - N\ln\frac{N}{m-N} \\ &\approx m\ln(1+\frac{N}{m}) - N\ln\frac{N}{m}(1+\frac{N}{m}) \\ &\approx N - N\ln\frac{N}{m} \end{aligned} \tag{25}$$

and therefore we obtain for S

$$S \approx k(N - N\ln\frac{N}{m}) \tag{26}$$

When the volume of the container is increased to V_b, the number of possible states in the container also increases from m to xm, where $x = \frac{V_b}{V_a}$. Then the entropy is given by

$$S' \approx k(N - N\ln\frac{N}{xm}) \tag{27}$$

and the entropy change is given by

$$\Delta S = S' - S \approx kN\ln x \tag{28}$$

Converting it to the mole number, n, and universal gas constant R, it follows that

$$\Delta S \approx nR\ln\frac{V_b}{V_a}. \tag{29}$$

Note that this result is the same as the entropy change we obtained for a reversible isothermal process. And in general, one can show that the entropy change of an irreversible process can be approximated as if it was a reversible process under most similar conditions (here: constant T).

8.6.2 Special Example: Entropy of mixing

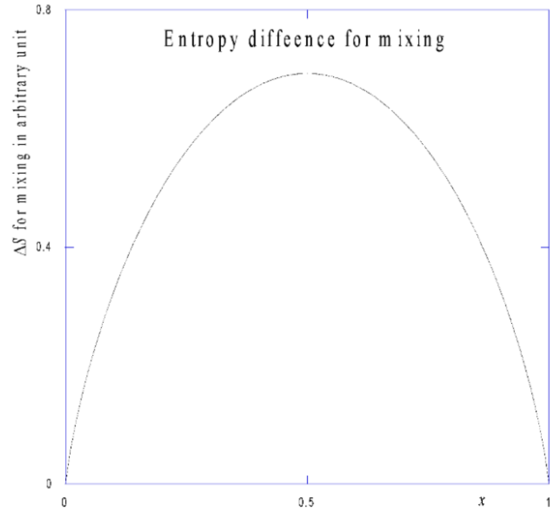
A thermally isolated container with a volume V is split into two, $V_1 = xV$ and $V_2 = (1-x)V$ where $0 \leq x \leq 1$, separated by a thermally isolated wall. They are filled with two different ideal gasses of $n_1 = xn$-mol and $n_2 = (1-x)n$-mole, respectively. Both gasses have the same pressure, $P_1 = P_2 \equiv P$, and the same temperature, $T_1 = T_2 \equiv T$. Now we remove the wall, and gas-1 expands into volume-2 and gas-2 into volume-1 (see last figure of this section).

Since there is no temperature difference between the two regions, the temperature remains constant in this process. The two gases do not perform any work either, since they have nothing to move mechanically when they expand. Therefore, this process can be dealt as two gases making a free expansion process independently. Then the entropy changes of the two gases are given by

$$\Delta S_1 = xnR\ln\frac{V}{xV} \quad \text{and} \quad \Delta S_2 = (1-x)nR\ln\frac{V}{(1-x)V} \tag{30}$$

and the total entropy change can be expressed as

$$\Delta S = \Delta S_1 + \Delta S_2 = xnR\ln\frac{V}{xV} + (1-x)nR\ln\frac{V}{(1-x)V} = -nR[x\ln x + (1-x)\ln(1-x)] \tag{31}$$



As seen from the figure above, where $\Delta S = 0$ at $x = 0$ and $= 1$, i.e. with one gas and no mixing, and maximum at x = 0.5, i.e. mixing of two equal amount of gasses. This makes sense for two different ideal gases, since the mixing of two different gasses is an irreversible process. However, if the two gasses are completely identical, i.e. gas molecules are indistinguishable, no change occurs after removing the wall. The original state can be restored by simply putting back the wall, thus ΔS must be $= 0$, which is not in agreement with the result above. This depends on how to interpret "distinguishable" and "indistinguishable" and their statistical treatment showing a limitation of classical thermodynamics description.