

1 Introduction to Thermodynamics

Thermodynamics aims to quantitatively describe systems using measurable macroscopic properties. It seeks to relate heat, work, and temperature to energy, entropy, and the physical properties of matter. The description and understanding of chemical processes are fundamentally based on thermodynamics.

2 First Law of Thermodynamics

There exists a function U that describes the total energy of a system. The change in energy of a system is the sum of the heat (q) transferred to the system and the work (W) done on the system,

$$\Delta U = q + W. \quad (1)$$

We will discuss later more in detail, ΔU is a state function, while q and W are “path” or “process” functions, meaning they depend on the path from two values.

2.1 P-V work

In thermodynamics, one of the most common procedure to do work on a system is by changing its volume. Let's consider a gas trapped in a container where we can compress one of its walls using a piston, where P is the external pressure applied on the system. In physics, the work W done by a force \mathbf{F} during the displacement of the particles from x_i to x_f ,

$$W = \sum F(x)\Delta x, \quad \text{in the infinitesimal limit} \quad W = \int_{x_i}^{x_f} F(x)dx, \quad (2)$$

meaning that

$$dW = F(x)dx. \quad (3)$$

For this example, we can compute the pressure using $P = \frac{F}{A}$, where A is the piston's cross-sectional area. Therefore, we can define work as,

$$dW = PAdx. \quad (4)$$

For a piston with length ℓ , $\ell = b - x$ where x is piston's position and b is the end position. The volume of the container can be computed using $V = A\ell$, making $V = A(b - x)$. If we take the total differential of V we get,

$$dV = \left(\frac{\partial V}{\partial x} \right) dx = -Adx \quad (5)$$

If we combine Eq. 5 and Eq. 4, we get,

$$dW = -PdV \quad \text{only for closed systems} \quad (6)$$

- Contraction on the system, $dV < 0$,

$$dW = -PdV = (-)(+)(-) \rightarrow dw > 0 \quad (7)$$

- Expansion on the system, $dV > 0$,

$$dW = -PdV = (-)(+)(+) \rightarrow dW < 0 \quad (8)$$

Let's consider an infinite number of successive infinitesimal changes in the piston, all at a constant pressure. The total work done on the system is,

$$\sum_i W_i = \sum_i -P\Delta V_i \rightarrow W = - \int_i^f PdV \quad (9)$$

Gas compression:

The most common example of reversible compression to do work on the system is the piston, Fig. 1. Where in a container one traps some gas and we are only able to “move” one of the walls of the container using a piston. A is the cross-sectional area, ℓ is the length of the container, b is the of the fixed end of the system and x is the piston's position.

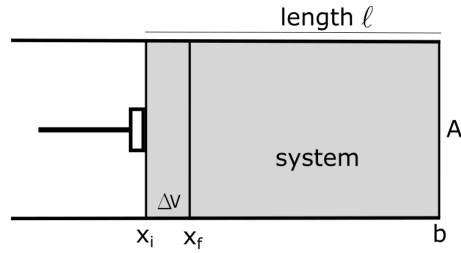


Figure 1: Compression of a gas with a piston.

If applied pressure P is constant we can compute the work done on the system using the definition of work, Eq. 9.

$$\begin{aligned} W &= - \int_{V_i}^{V_f} PdV = -P \int_{V_i}^{V_f} dV = -PV \Big|_{V_i}^{V_f} = PV_i - PV_f \\ &= P(Ab - Ax_i) - P(Ab - Ax_f) = PA(x_f - x_i). \end{aligned} \quad (10)$$

For this to be valid we assumed that P was constant at all times.

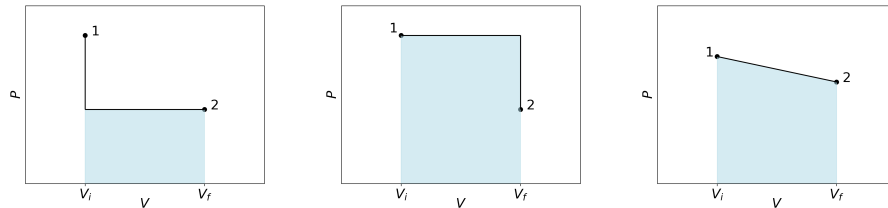


Figure 2: The work done by the system for three different processes.

There isn't a restriction for Eq. 9 to only be valid for constant pressure. P is a function of its temperature and volume, $P = P(T, V)$, meaning,

$$W_{rev} = - \int_{V_i}^{V_f} P(T, V) dV, \quad (11)$$

for example, for an ideal gas $P = nR\frac{T}{V}$, making $W_{rev} = -nR \int_{V_i}^{V_f} \frac{T}{V} dV$. Eq. 9 is known as **line integral**, and from its definition w_{rev} is the integral, area under the curve of $P(T, V)dV$. Fig. 2 illustrates some of the different possible “trajectories” or “paths” that can do work on the system, all three have the same initial P_i, V_i and final P_f, V_f state, yet they do different work on the system. Processes where the pressure is held constant are called **isochoric**, and processes where the volume is held fixed are named **isobaric**. Two of the diagrams in Fig. 2 depend on these types of processes.

2.2 Heat

One of the other important components in thermodynamics is **heat**. Heat is not a state function, as it depends on the “path” between two states. The concept of heat is energy that flows in between two objects that have different temperatures. As you may have noticed in real life, after some times two objects at unequal temperatures will reach a thermal equilibrium, meaning same final temperature. Experimentally one can observe the following,

$$m_2 c_2 (T_2 - T_f) = m_1 c_1 (T_f - T_1) = q, \quad (12)$$

where m_i is the mass of the object i , and c_i is the **specific heat capacity** of the object i . q is the amount of **heat** that flowed from 2 to 1; $T_2 > T_f > T_1$. The heat capacity of a material is an important property as it determines the response of a material to heat flow to or from the system. Part of the reason life exists on earth is because of the value of water’s heat capacity.

In the limit of an infinitesimal flow of heat at constant pressure, we can define,

$$dq_p = mc_P dT = C_P dT, \quad (13)$$

where c_P is the heat capacity of a substance at constant pressure, $C_P = mc_P = \frac{dq_p}{dT}$. Later in this lecture we will see that this is related to a state function called Enthalpy. A more accurate version of Eq. 12 is,

$$m_2 \int_{T_f}^{T_2} c_{P_2}(T) dT = m_1 \int_{T_1}^{T_f} c_{P_1}(T) dT = q_P, \quad (14)$$

Exercise: What is the ΔU for the process of heating 1mol of water from room temperature (25C) to 30C, all at 1 atm pressure. We know that $\Delta U = q + w$. Let’s compute each separately.

$$q_P = mC_P \Delta T = (18g) \left(1 \frac{\text{cal}}{\text{gC}} \right) (30 - 25) = 90\text{cal} \quad (15)$$

$$W = - \int_{V_i}^{V_f} P dV = -P(V_f - V_i) = -P\Delta V, \quad (16)$$

we should remember that the volume of an object changes at different temperatures, so we can relate $V = \frac{m}{\rho(T)}$, where $\rho(T)$ is the density of water at temperature T ; $\rho(25C) = 0.9970 \frac{\text{g}}{\text{cm}^3}$ and $\rho(30C) = 0.9956 \frac{\text{g}}{\text{cm}^3}$.

$$W = -P(V_f - V_i) = -(1\text{atm}) \left(\frac{18g}{0.9956 \frac{\text{g}}{\text{cm}^3}} - \frac{18g}{0.9970 \frac{\text{g}}{\text{cm}^3}} \right) \approx -0.0006\text{cal}. \quad (17)$$

We can use the following change of units $1\text{cm}^3\text{atm} = 0.02421\text{cal}$. If we combine both calculations, we get that $\Delta U \approx q_p = 90\text{cal}$.

Exercise: Consider one mol of air gas undergoing a thermal expansion. The initial and final pressure are, 200 kPa and 100 kPa. The temperature of this process is 50 C and we can assume it follows the ideal gas law. What is the work done?

$$\begin{aligned}
 W &= - \int_{V_i}^{V_f} P dV = - \int_{V_i}^{V_f} \underbrace{\frac{nRT}{V}}_{PV=nRT} dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln(V) \Big|_{V_i}^{V_f} \\
 &= -nRT \ln \frac{V_f}{V_i} = nRT \ln \frac{P_i}{P_f} = \left(8.314 \frac{J}{kmol} \right) (273.15 + 50) \ln \frac{200}{100} = -1.86 J \quad (18)
 \end{aligned}$$

This indicate that $W < 0$ which means that work is done on the system.

3 Second Law of Thermodynamics

The **entropy** of a system (S) and its surroundings, together, always increases, $\Delta S > 0$. We can relate entropy with the heat of a process using the following equation,

$$dq = TdS. \quad (19)$$

Commonly, we true second law of thermodynamics means that,

$$\Delta S_{sys} + \Delta S_{surr} > 0, \quad (20)$$

meaning the entropy of the universe always increases.

3.1 Clausius Theorem

On of the main consequences of Eq. 20 is the relationship between heat of the system (q_{sys}) and entropy,

$$dS_{sys} \geq \frac{dq}{T_{surr}} \quad \text{or} \quad dq \leq T_{surr} dS_{sys} \quad (21)$$

where dq is the infinitesimal heat that is taken from the reservoir and absorbed by the system, $dq > 0$. If dq was negative, meaning the system transfer heats to the surrounding dS_{sys} will be negative, which violates the second law of thermodynamics (Eq. 20). This indicates why heat flows from hot to cold objects.

3.2 Entropy

From the first law of thermodynamics, we defined a stat function U which was the internal energy. Entropy is the sate function that drives the second law of thermodynamics, unfortunately entropy is a function that describes microscopic states

- Temperature (T) \rightarrow measure of the average molecular energy.
- Internal energy (U) \rightarrow total molecular energy.
- Entropy (S) \rightarrow measure of the molecular disorder of a molecular state.

For a mathematical formulation of entropy, S of a system is a function of the probability p of the system's state,

$$S = f(p). \quad (22)$$

Entropy is a state function and an extensive property, so for a system with “two” components,

$$S = S_1 + S_2 \quad \rightarrow \quad h(p_{12}) = f(p_1) + g(p_2), \quad (23)$$

where h , f , and g are three different functions.

We are gonna consider the description of the following “system”, in a container we have 4 atoms of the same type, Fig. 3. At the beginning of the experiment, using an “invisible” barrier that also prohibits the exchange of heat we place all 4 atoms are in the left of the container. Fig. 3 lists all possible states and the number of times each will appear.

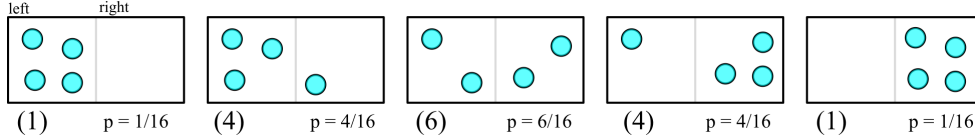


Figure 3: All possible states for a container filled with 4 atoms.

Using basic probability we can compute the probabilities listed in Fig. 3. First we start with the probability that each atom is either in the left or right part of the container,

$$P_{atom}(x_L) = P_{atom}(x_R) = \frac{1}{2} \quad (24)$$

For two atoms we can ask, what is the probability that both are in the left or right part of the container,

$$P_{atom}(x_L(1), x_L(2)) = P_{atom}(x_R(1), x_R(2)) = \frac{1}{2} \cdot \frac{1}{2}, \quad (25)$$

we can do these for N atoms for each type,

$$P_{atom}(x_R(1), \dots, x_R(N)) = \prod_{i=1}^N \left(\frac{1}{2}\right) \quad \text{or} \quad P_{atom}(x_L(1), \dots, x_L(N)) = \prod_{i=1}^N \left(\frac{1}{2}\right) \quad (26)$$

Then, we remove the “invisible” barrier and after a while we get to the maximum, all types of atoms equally distributed in the container. If we didn’t know anything about entropy and we were asked “what do you think it will happen?”. The majority of the answers will be that the atoms diffused in the container and probably we will find two atoms in each side of the container, Fig. 3.

The probabilities of all possible states, Fig. 3, can be computed using the monomial distribution,

$$P(X = k) = \binom{N}{k} p^k (1 - p)^{N-k}, \quad (27)$$

where, $P(X = k)$ is the probability of having k atoms in the left part of the container, $\binom{N}{k}$ is the binomial coefficient ($\binom{N}{k} = \frac{N!}{k!(N-k)!}$), p is $P_{atom}(x_L)$, and $(1 - p) = P_{atom}(x_R)$. N is the number of atoms.

Listing. 1 shows the lines of code to compute all the probabilities.

```

1 import numpy as np
2 from scipy.stats import binom
3
4 n = 4 # total number of atoms
5 p = 0.5 # prob of being in the left
6 k = # number of atoms in the left
7 print(binom.pmf(k, n, p))

```

Listing 1: Binomial distributio

Look at Eq. 28 and Eq. 25 and think of a function that can transform

$$\text{product} \rightarrow \text{sum}$$

If you recall the laws of logarithms, $\log(xy) = \log(x) + \log(y)$, therefore, we can define Eq. 28 using the natural logarithm,

$$f(p_i) = k \ln(p_i) \quad (28)$$

where k is a constant that must be the same for all systems also known as the **Boltzmann's constant**.

Since entropy is a state function,

$$\Delta S = S_1 - S_2 = k \ln(p_2) - k \ln(p_1) = k \ln \frac{p_2}{p_1}, \quad (29)$$

where the probability of the initial (p_1) and final (p_2) states can be computed using Eq. 26. Let's assume the target final state is the one with two atoms in each side of the container, $p_2 = \frac{6}{16} = 0.375$. Therefore the entropy change from the initial to the final state is, Since entropy is a state function,

$$\Delta S = S_1 - S_2 = k \ln \frac{p_2}{p_1} = k \ln \frac{\frac{6}{16}}{\frac{1}{16}} = k \ln \frac{6 \cdot \cancel{16}}{1 \cdot \cancel{16}} = k (\ln(6) - \ln(1)) \quad (30)$$

$$= k \ln(6) > 0 \quad (31)$$

From these exercise, we can see that $\Delta S > 0$, meaning that this process is **spontaneous**. If we consider the opposite processes, $\Delta S < 0$, meaning the process is **not spontaneous**, which aligns with how the world works.

If instead we consider a really large number of atoms, $N \sim 10^6$, we could ask, what is the probability of an initial state where all N atoms are in the left of the container and equally distributed in the container. For these two states we can use the Binomial distribution to compute the probabilities of these states,

$$p_1 = \left(\frac{1}{2}\right)^N. \quad (32)$$

Because of the large number of molecules $p_2 \gg p_1$, meaning $p_2 \approx 1$. Leading to,

$$\Delta S = S_1 - S_2 = k \ln \frac{p_2}{p_1} = k \ln 1 - k \ln \left(\frac{1}{2}\right)^N = Nk \ln 2, \quad (33)$$

$$\Delta S > 0, \quad (34)$$

also an spontaneous processes.

The magnitude of the entropy of a given process is not relevant, what matters is the sign,

- $\Delta S > 0 \rightarrow$ spontaneous process
- $\Delta S < 0 \rightarrow$ not spontaneous process

We can combine the first and second law of thermodynamics to understand the nature of a process,

$$dU = dq + dW = TdS - PdV \quad (35)$$

we can rearrange this equation in the following way,

$$dS = \frac{dU}{T} + \frac{PdV}{T} \quad (36)$$

if

- $\Delta S > 0 \rightarrow$ irreversible transformation
- $\Delta S = 0 \rightarrow$ reversible transformation
- $\Delta S < 0 \rightarrow$ forbidden transformation

Eqs. 35 and 36 are known as the differential statements of the first and second law of thermodynamics, and combined with $dS > \frac{\delta q}{T}$, are the pivotal equations of thermodynamics.

4 Other state functions

Because of the complexity of experimental set ups where we lack the ability to manipulate energy or entropy, we have to define other state functions that can help us understand the nature of processes. In thermodynamics, there are many possible state functions that one can define, and these are commonly a function of internal energy, volume, pressure and volume.

4.1 Enthalpy

Enthalpy is defined as,

$$H = U + PV. \quad (37)$$

Since P , V , and U are all state functions, H is a state function. Why do we choose this definition?. Let's compute ΔU at constant pressure,

$$U_2 - U_1 = q + W = q - \int_{V_1}^{V_2} PdV = q_P - P(V_2 - V_1). \quad (38)$$

$$q_P = U_2 + PV_2 - U_1 - PV_1 = H_2 - H_1, \quad (39)$$

$$q_P = \Delta H. \quad (40)$$

Enthalpy is the heat absorbed at constant pressure.

We can do a similar procedure for the internal energy but at constant volume,

$$U_2 - U_1 = q + W = q - \int_{V_1}^{V_2} PdV = q_V. \quad (41)$$

$$q_V = \Delta U. \quad (42)$$

The internal energy is the heat absorbed at constant volume. From this expression we can also deduct that, for an isothermic and isobaric process, $\Delta U = 0$, since $q_V = C_V dT$, and $dT = 0$.

Using the definition of heat capacity, Eq. 13, and the formula of total differential we can find the following relations. Let's define $U = U(T, V)$ and $H = H(T, P)$, their total differentials are,

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \cancel{\left(\frac{\partial U}{\partial V}\right)_T dV} \quad \text{at constant volume} \quad dU = \left(\frac{\partial U}{\partial T}\right)_V dT \quad (43)$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \cancel{\left(\frac{\partial H}{\partial P}\right)_T dP} \quad \text{at constant pressure} \quad dH = \left(\frac{\partial H}{\partial T}\right)_P dT \quad (44)$$

if we rearrange the equations we get that,

$$\left(\frac{\partial U}{\partial T}\right)_V = \frac{dU}{dT} = C_V \quad (45)$$

$$\left(\frac{\partial H}{\partial T}\right)_P = \frac{dH}{dT} = C_P. \quad (46)$$

The heat capacity of a processes carried at constant pressure is related to the change in the enthalpy, and heat capacity of a processes carried at constant volume is related to the change in the internal energy.

4.2 Helmholtz Free Energy

The Helmholtz free energy is defined as,

$$A = U - TS \quad (47)$$

where using Eq. 35, we get

$$dA = dU - d(TS) = dq + dW - d(TS) \quad (48)$$

$$\leq TdS - PdV - (SdT + TdS) \quad (49)$$

$$dA \leq -SdT - PdV \quad (50)$$

The change in the Helmholtz energy is directly related to the change in temperature and the change in volume.

If we consider a process at constant pressure and volume we get,

$$dA \leq 0 \quad (51)$$

This transformation will occur in a finite period of time only if the final state has a lower Helmholtz energy.

Exercise Let's demonstrate Eq. 50.

$$dA = dq + dW - d(TS) = dq + dW - SdT - TdS, \quad \text{let's solve for } dq \quad (52)$$

$$dq = dA - dW + SdT + TdS, \quad \text{let's use Eq. 21, } TdS \geq dq \quad (53)$$

$$TdS \geq dq = dA - dW + SdT + TdS, \quad (54)$$

$$TdS \geq dA - dW + SdT + TdS, \quad \text{let's rearrange this equation} \quad (55)$$

$$dA \leq \cancel{TdS} + dW - SdT - \cancel{TdS} = dW - SdT, \quad (56)$$

if we define $dW = -PdV$, then $dA \leq -PdV - SdT$.

4.3 Gibbs Free Energy

The Gibbs free energy is defined as,

$$G = H - TS \quad (57)$$

where using Eqs. 37 and 47 we get,

$$G = U + PV - TS = A + PV \quad (58)$$

$$dG = dA + d(PV) \leq -SdT - PdV + PdV + VdP \quad (59)$$

$$dG \leq -SdT + VdP \quad (60)$$

If we consider a process at constant pressure and temperature we get,

$$dG \leq 0 \quad (61)$$

This transformation will occur in a finite period of time only if the final state has a lower Gibbs energy.

4.4 Gibbs equations

We can relate all the previous equations for each state function,

$$dU = TdS - PdV \quad (62)$$

$$dH = TdS + VdP \quad (63)$$

$$dA = -SdT - PdV \quad (64)$$

$$dG = -SdT + VdP \quad (65)$$

These equations are only valid for closed system and for P-V work.

The beauty of Gibbs equations is that we can relate them to properties, for example, let's define $U = U(S, V)$. The total differential of this function is,

$$dU = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV, \quad (66)$$

where from Eq. 62 we get that

$$\left(\frac{\partial U}{\partial S} \right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V} \right)_S = -P \quad (67)$$

Thermodynamics was built to express properties that are difficult to measure in terms of easily measured properties