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,

$$\Delta U = Q + W. \tag{1}$$

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,

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

meaning that

$$dw = F(x)dx. \tag{3}$$

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,

$$dw = PAdx. \tag{4}$$

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,

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

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

$$dw = -PdV \quad \text{only for closed systems} \tag{6}$$

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

$$dw = -PdV = (-)(+)(-) \rightarrow dw > 0 \tag{7}$$

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

$$dw = -PdV = (-)(+)(+) \rightarrow dw < 0 \tag{8}$$

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

$$\sum_i W_i = \sum_i -P\Delta V_i \rightarrow W = -\int_i^f pdV \tag{9}$$

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.
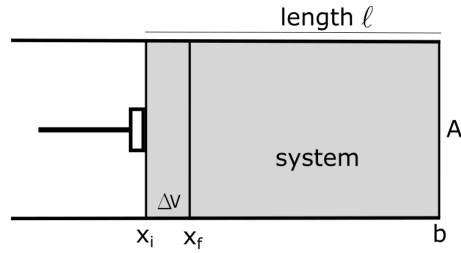

Figure 1: Compression of a gas with a piston.

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

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

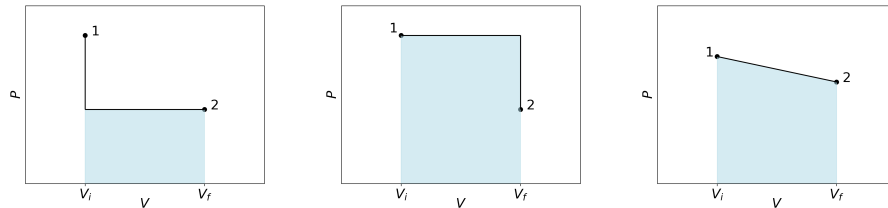For this to be valid we assumed that P was constant at all times.

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,

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

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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 it's definition w_{rev} is the integral, area under de 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 the 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,

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

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,

$$dq_p = mc_P dT = C_P dT, \tag{13}$$

where c_P is the heat capacity of a substance at constante 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,

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

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

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

$$w = -\int_{V_i}^{V_f} PdV = -P(V_f - V_i) = -P\Delta V, \tag{16}$$

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; $\rho(25C) = 0.9970\frac{g}{cm^3}$ and $\rho(30C) = 0.9956\frac{g}{cm^3}$.

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

We can use the following change of units $1cm^3atm = 0.02421cal$.

If we combine both calculations, we get that $\Delta U \approx q_p = 90cal$.

3 Enthalpy

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. **Enthalpy** is defined as,

$$H = U + PV. \tag{18}$$

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,

$$U_2 - U_1 = q + w = q - \int_{V_1}^{V_2} PdV = q_P - P(V_2 - V_1). \tag{19}$$

$$q_P = U_2 + PV_2 - U_1 - PV_1 = H_2 - H_1, \tag{20}$$

$$q_P = \Delta H. \tag{21}$$

Enthalpy is the heat absorbed at constant pressure.

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

$$U_2 - U_1 = q + w = q - \int_{V_1}^{V_2} PdV = q_V. \tag{22}$$

$$q_V = \Delta U. \tag{23}$$

The internal energy is the heat absorbed at constant volume.

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,

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad \text{at constant volume} \quad dU = \left(\frac{\partial U}{\partial T}\right)_V dT \tag{24}$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad \text{at constant pressure} \quad dH = \left(\frac{\partial H}{\partial T}\right)_P dT \tag{25}$$

if we rearrange the equations we get that,

$$\left(\frac{\partial U}{\partial T}\right)_V = \frac{dU}{dT} = C_V \tag{26}$$

$$\left(\frac{\partial H}{\partial T}\right)_P = \frac{dH}{dT} = C_P. \tag{27}$$

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.