

Thermodynamics

Grau en Enginyeria Matemàtica i Física

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Second Quatrimester 2023-24

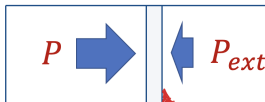
2. First law.

2.1. PV Work

Expansion-compression work

Mechanical work is a way of exchanging energy between the system and its surroundings. The key to correct interpretation is to clearly identify **who does the work and who receives it**.

Consider the system in the figure:



When we release the piston from the stopper, there will be a displacement to the right of the piston to a new equilibrium position. What is the mechanical work done by/on the system?

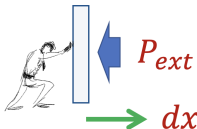
We will consider the *physical* signs convention: **What enters the system is positive and what comes out, negative.**

2.1. PV Work

Expansion-compression work

We consider the pressure of the system to be P and that of the surroundings, P_{ext} , with $P > P_{ext}$.

In the process of movement (displacement) of the frictionless piston, the external agent against which the system does work is the external pressure.



Therefore, we can identify **the work done by the piston on the system** as

$$dW = -Fdx = -P_{ext}Adx = -P_{ext}dV \quad (1)$$

The work done on/by the system is defined by the external pressure (the controlling parameter).

2.1. PV Work

Examples

Expansion against $P_{\text{ext}} = \text{const.}$

Assume that the system expands from an initial volume V_i to a final volume V_f . The work will simply be

$$W = - \int_{V_i}^{V_f} dV P_{\text{ext}} = -P_{\text{ext}} \int_{V_i}^{V_f} dV = -P_{\text{ext}} (V_f - V_i)$$

Questions:

- ▶ Is the process quasistatic?
- ▶ Is the process reversible?
- ▶ What would the work done by the system be if the external pressure were zero?

2.1. PV Work

Examples

Reversible expansion of an ideal gas at constant temperature.

Let us now assume that the system is an ideal gas that satisfies Boyle's law (Boyle - Mariotte).

For the process to be reversible, we must carry it out quasi-statically. In addition, releasing the system from the stopper should trigger no change. Since our control variable is the external pressure, we will have to do the following process:

- ▶ Increase the external pressure until it becomes equal to the internal pressure, before removing the stopper. Then, remove the stopper.
- ▶ We will then lower the external pressure little by little until the piston reaches the position for the desired final system volume. The intermediate states are all in equilibrium and, therefore, the external pressure is equal to that of the gas at all times (red equal-sign below).

$$W^{rev} = - \int_{V_i}^{V_f} dV P_{ext} = - \int_{V_i}^{V_f} dV P(T, V)$$

2.1. PV Work

Examples

Reversible expansion of an ideal gas at constant temperature.

If the gas is ideal and the walls are diathermal (heat conducting), we can write

$$W = - \int_{V_i}^{V_f} dV P(T, V) = - \int_{V_i}^{V_f} dV \frac{NRT}{V}$$

Since the external temperature is constant, and the system is always in equilibrium, NRT is independent of the volume, and it can come out of the integral, resulting in

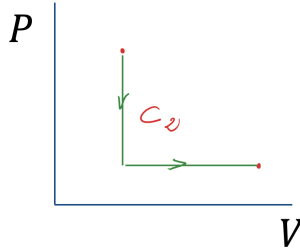
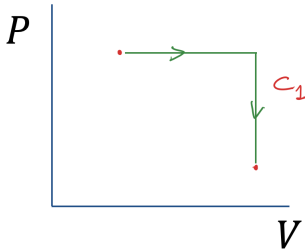
$$W = - \int_{V_i}^{V_f} dV \frac{NRT}{V} = -NRT \ln \left(\frac{V_f}{V_i} \right)$$

- ▶ What would be the reversible work of expansion of a van der Waals gas?
- ▶ Does the same expression above work also for a compression, instead or only for an expansion?

2.1. PV Work

General aspects

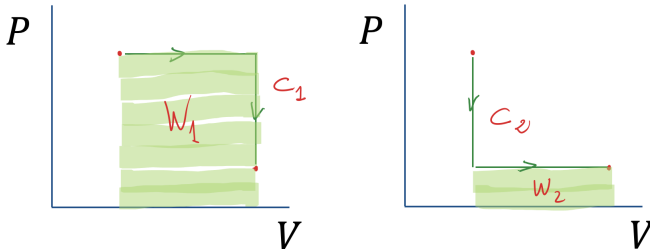
- ▶ In many cases we will be able to calculate the work directly, even if the process is irreversible or not quasi-static, because it is a formula that comes from mechanics itself.
- ▶ **Between two equilibrium states, the work done in a process depends on the path** followed to get from one to the other.



2.1. PV Work

General aspects

- ▶ In many cases we will be able to calculate the work directly, even if the process is irreversible or not quasi-static, because it is a formula that comes from mechanics itself.
- ▶ **Between two equilibrium states, the work done in a process depends on the path** followed to get from one to the other.



- ▶ Work is not a state variable. The question *which work does this equilibrium state have?* is absurd.

2.1. PV Work

Measurability of internal energy U

The concept of work leads us to the identification of the internal energy of the system as *state function*, that is to say, defined in the states of equilibrium, as we had previously stated. This is only the experimental confirmation of its existence and measurability:

Isolated systems (surrounded by adiabatic walls) have the property that the work done between an initial state (i) and a final state (f) is independent of the path and depends only on the initial and final states.

Therefore, we will say that this work, which *a priori* depends on the path, but in this case only depends on the initial and final states, *ergo* must be equivalent to the variation of a state function, which we call *internal energy*. This is the realization of its existence and measurability.

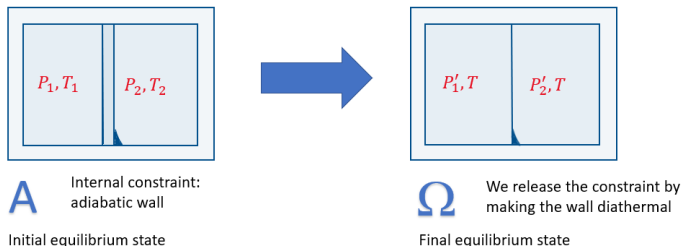
2.2. First law

Heat

We saw that we could change the state of a system by doing work on it, and that there is a state function U which is directly connected to the work done in an adiabatic transformation.

Then, since we have this state variable U , we can define *heat* as that form of changing the internal energy U which is not work.

Heat is therefore the energy that is transferred between two systems, initially at temperatures T_1 and T_2 (eg with $T_1 > T_2$), when they are brought into thermal contact.

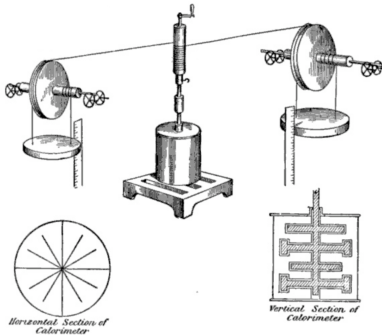


2.2. First law

Mensurability of heat

Since we associate it with internal energy, heat will have units of energy: Joule's paddle-wheel experiment or the equivalent of the calorie to mechanical work:

$$1 \text{ cal} = 4.18 \text{ J}$$



Joule's Water-Churning Apparatus for Determining the Mechanical Equivalent of Heat.

The experiment quantified the mechanical work on a body of water (system) that achieved the same result (raising T from a T_i to a T_f) as the transfer of heat. The work was performed by dropping the weights a known distance, using the potential energy to propel a paddle-wheel inside a water barrel (under adiabatic conditions). The second International Congress honored him with the use of his name for the Joule. (For a historical account of the experiment, see M.H. Shamos, *Great Experiments in Physics*.)

► Is the work reversible?

2.2. First law

Mensurability of heat

We can say that heat is, intuitively, what we transfer to the system by *heating or cooling*. Therefore, we associate heat primarily with a change in temperature.

This notion is transferred to the concepts of heat capacity. We will define **heat capacity at constant volume** as the heat transferred to the system keeping $V = \text{constant}$.

$$\left. \frac{dQ}{dT} \right|_V = C_V(T, P, N) = m(N) c_V(T, P)$$

c_V is the heat capacity per unit mass.

Then, in a constant volume process, the heat transferred can be calculated from the heat capacity and the temperature difference achieved,

$$Q_V = \int_{T_1}^{T_2} dT' C_V(T', P(T', V), N)$$

2.2. First law

Mensurability of heat

We can also define the heat capacity at constant pressure in an analogous way,

$$\left. \frac{dQ}{dT} \right|_P = C_P(T, P, N) = m(N) c_P(T, P)$$

In the same way, in a heating process at constant pressure between two temperatures, we will have

$$Q_P = \int_{T_1}^{T_2} dT' C_P(T', P, N)$$

2.2. First law

Statement of the First Law

After the work of Julius Robert von Mayer (1842), Rudolf Clausius (1850) announced the First Law of Thermodynamics as we know it today [4],

$$\Delta U = Q + W \quad \text{First Law of Thermodynamics} \quad (2)$$

This equation refers to the variation of U in a process between an initial state and a final one: It applies to processes but not to states. However, ΔU will depend only on the initial and final states. Therefore, whereas Q and W will depend on the process, their sum will only depend on the initial and final states.

2.2. First law

Some consequences

Work in an adiabatic expansion

If we assume that the system is thermally isolated, the amount of heat flowing in a process is $Q = 0$. Then,

$$\Delta U = W$$

When we talked about the measurability of internal energy, we referred to the fact that the First Law allows us to calculate its variation in an adiabatic process.

Heat at constant volume

Since the expansion-compression work is $dW = -PdV$, if the volume does not change, the system does no work (receives no work). Then,

$$\Delta U = Q$$

If we now take the definition of heat capacity at constant volume, using the First Law with $\Delta U = Q$ we can write,

$$C_V = \left. \frac{dQ}{dT} \right|_V = \left. \frac{\partial U}{\partial T} \right|_V$$

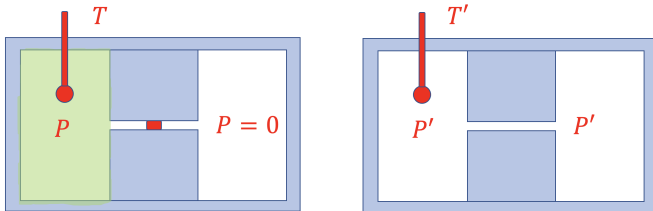
2.2. First law

Some consequences

Joule's experiment

This suggests that if we knew the function $U(T, V, N)$ its derivative with respect to T at constant V and N would give us the heat capacity. Therefore, by knowing the function $C_V(T, V, N)$ we can infer what the function U looks like with respect to variations in the system temperature, which will be another state function. Note that so far we only have Boyle's equation, obtained experimentally.

Joule proposed an adiabatic expansion of a gas against a vacuum, and measured its temperature variation.



2.2. First law

Some consequences

Joule's experiment

In the case of ideal gases, what is found experimentally is that the final temperature is equal to the initial one; that is to say, that there is no variation in temperature.

According to the First Law, since the system does not change its volume and does not exchange heat,

$$\Delta U = W + Q = 0$$

Then, if we write U as a function of T and V , we will have:

$$dU = \left. \frac{\partial U}{\partial T} \right|_V dT + \left. \frac{\partial U}{\partial V} \right|_T dV = 0$$

2.2. First law

Some consequences

Joule's experiment

This, applied to the left-side subsystem, implies that the temperature variation due to the expansion (volume variation of the left-side subsystem) is related to properties of the function $U(T, V)$ for the system in question, i.e.

$$\left. \frac{dT}{dV} \right|_U = - \frac{\left. \frac{\partial U}{\partial V} \right|_T}{\left. \frac{\partial U}{\partial T} \right|_V}$$

Joule finds that, for the ideal gas,

$$\left. \frac{dT}{dV} \right|_U = 0 \Rightarrow \left. \frac{\partial U}{\partial V} \right|_T = 0 \Rightarrow U(T, V) = N\phi(T) \quad (3)$$

Where $\phi(T)$ **is a function of the temperature only**. This is a new **equation of state** for the ideal gas.

2.2. First law

Some consequences

Joule's experiment

To determine ϕ , we note that

$$C_V = \left. \frac{\partial U}{\partial T} \right|_V = N \frac{d}{dT} \phi(T)$$

Then, for ideal gases we will have:

General ideal gas

$$U(T, N) = \int_{T_{ref}}^T dT C_V(T, N) + U(T_{ref}, N);$$

(4)

Simple ideal gases (Ar, N₂, etc.)

$$U = \frac{3}{2} NRT \text{ Monatomic}$$

$$U = \frac{5}{2} NRT \text{ Diatomic at low } T$$

2.2. First law

Enthalpy

Enthalpy is a **state function** derived from those we know, and which is useful, as will be seen. It is defined as

$$H = U + PV \quad (5)$$

In connection to the First Law, in a **reversible process**, we can say that

$$dH = dU + PdV + VdP = dW + dQ + PdV + VdP = dQ + VdP$$

Then, in a constant-pressure process

$$dH|_P = dQ|_P$$

Similarly to earlier, heat capacity at constant pressure is directly connected to enthalpy, then

$$C_P = \left. \frac{dQ}{dT} \right|_P = \left. \frac{\partial H}{\partial T} \right|_P$$

2.2. First law

Enthalpy

The specific heats at constant pressure and at constant volume are related. We can start from the definition of C_P ,

$$C_P = \left. \frac{\partial H}{\partial T} \right|_P = \left. \frac{\partial U}{\partial T} \right|_P + P \left. \frac{\partial V}{\partial T} \right|_P$$

The term in red is not C_V , because the variable we keep constant is P and not V (**Very important!**). Then, considering U as $U(T, V)$, we will have

$$dU = \left. \frac{\partial U}{\partial T} \right|_V dT + \left. \frac{\partial U}{\partial V} \right|_T dV \Rightarrow \left. \frac{\partial U}{\partial T} \right|_P = \left. \frac{\partial U}{\partial T} \right|_V + \left. \frac{\partial U}{\partial V} \right|_T \left. \frac{\partial V}{\partial T} \right|_P$$

Here, the term in blue is C_V . Therefore then,

$$C_P = C_V + \left[\left. \frac{\partial U}{\partial V} \right|_T + P \right] \left. \frac{\partial V}{\partial T} \right|_P$$

In the case of the ideal gas, this is called **Mayer's relation**. Here,

$$\left. \frac{\partial U}{\partial V} \right|_T = 0; \quad \left. \frac{\partial V}{\partial T} \right|_P = \frac{\partial}{\partial T} \left. \frac{NRT}{P} \right|_P = \frac{NR}{P}$$

Then,

$$C_P = C_V + NR$$

2.3. Cycles

Cyclic processes

It is important to see cyclic processes in relation to the First Law.

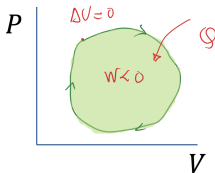
When a process is cyclic, its initial and final states are the same, and therefore all state functions are unchanged. This means that, in a cyclic process,

$$\Delta U|_{cycle} = 0$$

This does not mean that the system has not absorbed or released any heat, and not done or received any work, because the First Law only implies that

$$\Delta U|_{cycle} = 0 = Q + W \Rightarrow \boxed{Q = -W}$$

This is so because both heat and work are not state variables but path dependent.

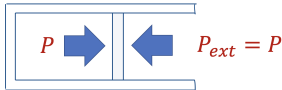


2.3. Cycles

Reversible adiabatic expansion

One of the most important classical processes is the adiabatic expansion-compression, as these occur in many practical situations and, moreover, are an important part of the Carnot cycle. The question we want to answer is: What is the work done in an adiabatic **reversible** expansion between a volume V_1 and a volume V_2 ? (for an ideal gas).

$$dQ = 0$$



$$dU = \left. \frac{\partial U}{\partial T} \right|_V dT + \left. \frac{\partial U}{\partial V} \right|_T dV = C_V dT$$

$$dU = dW^{\text{rev}} = -PdV$$

γ is the so-called coefficient of *adiabatic expansion*, factor of *isentropic expansion* or *adiabatic index*.

Equating,

$$C_V dT = -PdV = -\frac{NRT}{V} dV$$

$$\frac{C_V}{NR} \frac{dT}{T} = -\frac{dV}{V} \Rightarrow \frac{C_V}{NR} \ln \frac{T_f}{T_i} = -\ln \frac{V_f}{V_i}$$

$$\text{Then, } \left(\frac{T_f}{T_i} \right)^{\frac{C_V}{NR}} = \frac{V_i}{V_f} \Rightarrow \left(\frac{T_f}{T_i} \right)^{\frac{1}{\gamma-1}} = \frac{V_i}{V_f}$$

$$\text{on } \gamma \equiv \frac{C_P}{C_V}. \text{ Substituting, } T = \frac{PV}{NR} \text{ we obtain}$$

$$\frac{P_f}{P_i} = \left(\frac{V_i}{V_f} \right)^\gamma \text{ which is equivalent to } P_f V_f^\gamma = P_i V_i^\gamma$$

2.3. Cycles

Reversible adiabatic expansion

Reversible work in an adiabatic expansion/compression

We can now calculate the work in a reversible adiabatic expansion (or compression):

$$W = - \int_{V_i}^{V_f} dV P_{\text{ext}} = - \int_{V_i}^{V_f} dV P(V, T(V)) = - \int_{V_i}^{V_f} dV P_i V_i^\gamma \left(\frac{1}{V} \right)^\gamma$$

Integrating,

$$W = - \frac{1}{1-\gamma} P_i V_i^\gamma \left(V_f^{1-\gamma} - V_i^{1-\gamma} \right) = \frac{1}{1-\gamma} P_i V_i \left(1 - \left(\frac{V_f}{V_i} \right)^{1-\gamma} \right)$$

Unlike in an isothermal expansion, now the temperature varies with the volume, because we do not let heat flow between the system and its surroundings.

The change in internal energy will therefore be

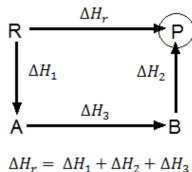
$\Delta U = W = \frac{1}{1-\gamma} P_i V_i \left(1 - \left(\frac{V_f}{V_i} \right)^{1-\gamma} \right)$. What will be the final temperature? If it is an expansion, will it be bigger or smaller than the initial one?

2.3. Cycles

Hess' law

Commonly, we need to know the heat released in a certain chemical reaction or in a change of state of the substances in a given process. Moreover, often, the reactions are carried out at constant pressure. In such case, we know that the heat absorbed or released in the process is equal to the change in enthalpy.

The big advantage is that, since enthalpy is a state function, it does not depend on the process but only on the initial and final states. Then, any process at constant pressure between these two states will have an identical enthalpy balance. This is, in essence, **Hess's law**.



2.3. Cycles

Definition of standard or normal states

The standard state refers to a pressure $P^\circ = 1 \text{ bar}$. The temperature has no standard, and must be specified separately. The standard states of substances are defined as the most stable form at the indicated temperature and standard pressure. For gases, the standard state is the *fictitious* state of an ideal gas.

The *standard* enthalpy of reaction ΔH_T° is defined as the change in enthalpy in the process of transforming a number of moles equal to the stoichiometric coefficients of pure reactants, each of them in its standard state at temperature T , into the number of moles that correspond to the stoichiometric coefficients of products under the same conditions.

The normal or standard enthalpy of formation of a pure substance $\Delta_f H_T^\circ$ is $\Delta_r H^\circ$ of the reaction in which 1 mol of this substance is formed from its element components. The reference form, as discussed, is the most stable form at standard pressure and temperature T . Obviously, the elements have a zero standard enthalpy of formation.

Recommended reading

- [1] I. Levine, *Principios de Fisicoquímica*, McGraw-Hill; Chapter 2. Calorimetry: §5.4
- [2] H.B. Callen, *Termodinámica*, Ediciones AC, Chap. 1.
- [3] https://ca.wikipedia.org/wiki/James_Prescott_Joule (2021)
- [4] https://en.wikipedia.org/wiki/First_law_of_thermodynamics (2021)