

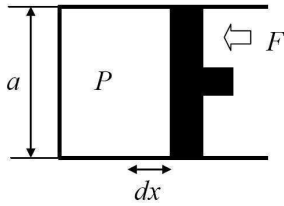
Chapter 3

Work, heat and the first law of thermodynamics

3.1 Mechanical work

Mechanical work is defined as an energy transfer to the system through the change of an external parameter. Work is the only energy which is transferred to the system *through* external macroscopic forces.

Example: consider the mechanical work performed on a gas due to an infinitesimal volume change (reversible transformation)



$$dV = -adx.$$

In equilibrium, the external force F is related to pressure P as

$$F = Pa.$$

For an infinitesimal process, the change of the position of the wall by dx results in performing work δW :

$$\begin{aligned}\delta W &= Fdx = -PdV, \\ \Rightarrow \delta W &= Padx.\end{aligned}$$

For a transformation of the system along a *finite* reversible path in the equation-of-state space (process with *finite* change of volume), the total work performed is

$$\Delta W = - \int_{V_1}^{V_2} PdV.$$

Note:

- Mechanical work is *positive* when it is performed *on* the system.
- δW is not an exact differential, i.e., $W(P, V)$ does not define any state property.
- ΔW depends on the path connecting $A (V_1)$ and $B (V_2)$.

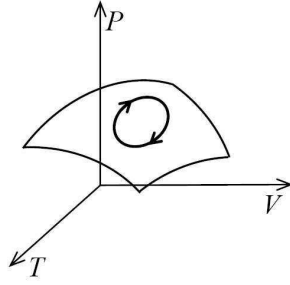


Figure 3.1: Cycle process.

Cycle process: during a *cycle process* the path in the equation-of-state space is a closed cyclic loop (Fig. 3.1); the work done in one cycle is the area enclosed:

$$W = - \oint P dV.$$

3.2 Heat transfer

An energy transfer in a system without changing any external parameter is called *heat transfer*. Heat transfer is a thermodynamic process that can be defined in the following way.

- 1) From the **atomic point of view**, it represents a transfer of energy in the form of thermal agitation of the constituent particles.
- 2) According to the **phenomenological definition**, it is an energy transfer imparted by a heating element (f.i, flame).

If a system absorbs an amount of heat ΔQ , its temperature rises *proportionally* by an amount ΔT :

$$\boxed{\Delta Q = C \Delta T}.$$

The proportionality constant C is called *heat capacity* of the substance (Wärmekapazität). It is an extensive quantity.

Specific heat c is defined as intensive heat capacity

per particle – C/N ,

per mole – C/n ,

or per unit volume – C/V .

Since heat transfer is a process independent of the system's particular state and ΔQ depends on the path connecting the initial and final states of the system, δQ is, therefore, not an exact differential and

$$\oint \delta Q \neq 0.$$

As an example of a process where only heat is transferred, let us consider two isolated systems with temperatures T_A and T_B such that $T_A > T_B$ (Fig. 3.2). The two systems

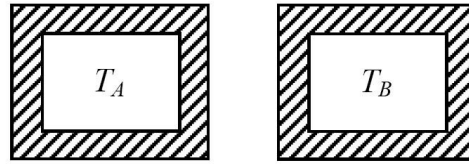


Figure 3.2: Isolated systems A and B .

are brought together without moving the wall between them (Fig. 3.3). Due to the

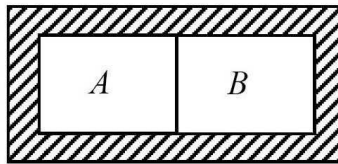


Figure 3.3: Systems A and B brought into thermal contact.

temperature difference, the energy is transferred through the static wall without any change of the systems' volume (no work is done). Under such conditions, the transferred energy from A to B is *heat*.

The unit of heat is *calorie*:

$$1 \text{ cal} \equiv 4.184 \text{ J.}$$

Since the heat absorbed by a body depends on the path of transformation, one can define various heat transfer processes:

- $T = \text{const}$ (isothermal process),
- $P = \text{const}$ (isobaric process),
- $V = \text{const}$ (isochoric process),
- $\Delta Q = 0$ (adiabatic process).

A corresponding subscript is used to distinguish the various types of paths. For example,

C_V – for heat capacity at constant volume,

C_P – for heat capacity at constant pressure.

Other thermodynamic coefficients that measure the linear response of the system to an external source are

- compressibility

$$\kappa = -\frac{1}{V} \frac{\Delta V}{\Delta P}$$

- the coefficient of thermal expansion

$$\alpha = \frac{1}{V} \frac{\Delta V}{\Delta T}.$$

Reminder: our convention is that

$$\delta Q > 0$$

when heat is transferred *to* the system

$$\delta W > 0$$

when work is done *on* the system with $\delta W = -PdV$.

3.3 First law of thermodynamics. Internal energy

The first law of thermodynamics expresses the *conservation of energy* principle by including heat as a form of energy.

- **Definition 1.** For a closed thermodynamic system, there exists a *function of state*, the *internal energy* U , whose change ΔU in any thermodynamic transformation is given by

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

where ΔQ is heat transferred to the system and ΔW is mechanical work performed on the system.

ΔU is independent of the path of transformation, although ΔQ and ΔW are path-dependent. Correspondingly, in a reversible infinitesimal transformation, the infinitesimal δQ and δW are not exact differentials (in the sense that they do not represent the changes of definite functions of state), but

$$\boxed{dU = \delta Q + \delta W}$$

is an exact differential.

- **Definition 2.** Energy *cannot* be created out of nothing in a closed cycle process:

$$\oint dU = 0 \quad \Rightarrow \quad \Delta Q = -\Delta W.$$

Microscopically, the *internal energy* is given by the sum of kinetic and potential energy of the constituent particles of the system

$$U = E = \frac{1}{2m} \sum_{i=1}^N p_i^2 + \sum_{i=1}^N \phi(\vec{r}_i) + \frac{1}{2} \sum_{i \neq j}^N V(\vec{r}_i - \vec{r}_j),$$

where $\phi(\vec{r}_i)$ is the external potential and $V(\vec{r}_i - \vec{r}_j)$ is the potential of interaction between particles (f. i., Coulomb interaction potential between charged particles).

Exercise: show that

$$U = \frac{3}{2} N k_B T = \frac{3}{2} n R T$$

for an ideal gas ($\phi(\vec{r}_i) = V(\vec{r}_i - \vec{r}_j) = 0$).

3.4 Energy and heat capacity for various processes

In this section we shall analyze various heat transfer processes and derive the corresponding heat capacities with the help of the first law of thermodynamics.

3.4.1 Isochoric process

An *isochoric process* is a constant volume process (Fig. 3.4).

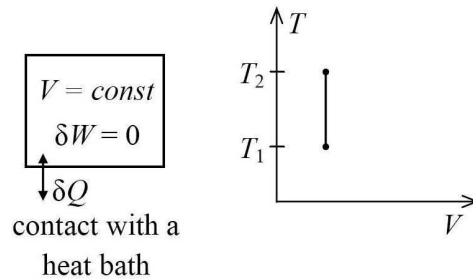


Figure 3.4: Isochoric process.

For such a process, it follows from the first law of thermodynamics that

$$dV = 0 \quad \Rightarrow \quad \delta W = 0$$

and

$$\boxed{\delta Q|_V = dU_V}.$$

We define the heat capacity at constant volume

$$\boxed{\left(\frac{\delta Q}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V = C_V}.$$

Let us derive the expression for C_V for an ideal gas. Its equation of state is

$$\boxed{PV = Nk_B T}. \quad (3.1)$$

Since thermodynamics does not assume the existence of atoms, we shall use the number of moles n (which is a chemical property of the substance) instead of the number of atoms N . Eq. (3.1) then reads

$$\boxed{Nk_B = nR},$$

with $R = 8.314 \times 10^7 \text{ Jmol}^{-1}\text{K}^{-1}$. The internal energy of an ideal gas is (as derived in the exercise)

$$U = \frac{3}{2}Nk_B T = \frac{3}{2}nRT.$$

Then,

$$dU = \frac{3}{2}nRdT \Rightarrow C_V = \frac{3}{2}nR,$$

and the heat capacity per mole at constant volume is

$$\frac{C_V}{n} = c_V = \boxed{\frac{3}{2}R}.$$

3.4.2 Isobaric process

An *isobaric process* is a constant pressure process (Fig. 3.5).

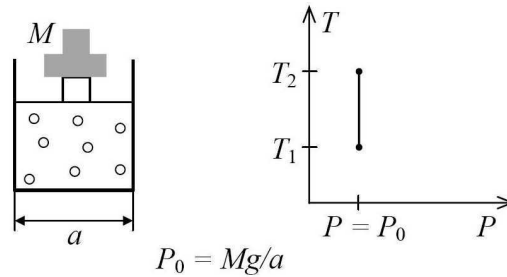


Figure 3.5: Isobaric process.

In order to find C_P we note that

$$\delta Q|_P = dU|_P + PdV|_P,$$

which, under an infinitesimal increment of temperature, is written as

$$\delta Q|_P = \left(\frac{\partial U}{\partial T}\right)_P dT + P \left(\frac{\partial V}{\partial T}\right)_P dT \equiv C_P dT.$$

Then,

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

For an ideal gas,

$$C_P = \frac{5}{2}nR = \frac{5}{2}Nk_B = (C_V + Nk_B).$$

3.4.3 Isothermal process

An *isothermal process* takes place at constant temperature.

Example: isothermal processes in an ideal gas (Fig. 3.6).

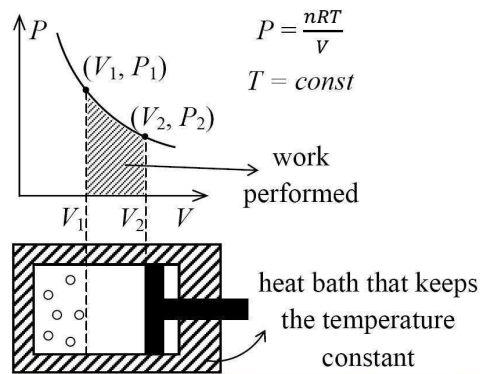


Figure 3.6: Isothermal process in an ideal gas.

During an isothermal process in an ideal gas, its pressure decreases with increasing volume. Work performed by the gas is (in general)

$$\Delta W = - \int_{V_1}^{V_2} dV P = \text{marked area in the } PV \text{ diagram.}$$

For an ideal gas,

$$\Delta W = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1} = -Nk_B T \ln \frac{V_2}{V_1}.$$

Since the internal energy $U = \frac{3}{2}nRT$ remains constant during the isothermal process, from the *first law of thermodynamics* it follows that

$$\Delta Q = -\Delta W,$$

the mechanical work performed by the system is given to the system as heat.

Note: heat *cannot* be transformed in work forever, this is NOT a periodic process. We will see that in the next chapter.

3.4.4 Free expansion of an ideal gas

Joule performed a classical experiment on free expansion consisting on the following: A thermally insulated ideal gas was allowed to expand freely into an insulated chamber, which had been initially empty (Fig. 3.7). After a new equilibrium state was established,

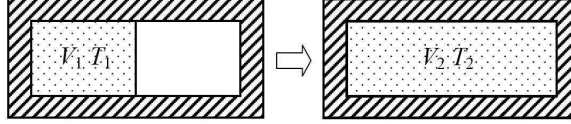


Figure 3.7: Free expansion of an ideal gas.

in which the gas fills both compartments, the final temperature of the gas was found to be the same as the initial one.

During such an expansion process no heat is transferred and no work is done:

$$\Delta W = 0,$$

$$\Delta Q = 0.$$

From the first law of thermodynamics it also follows that

$$\Delta U = 0.$$

Since $U = U_0 = \text{const}$, from the equation for $U(V, T)$ one can obtain the equation for $T(V, U = U_0)$, which is

$$T_2 = T_1 + \int_{T_1}^{T_2} \left(\frac{\partial T}{\partial V} \right)_U dV.$$

For an ideal gas,

$$U = \frac{3}{2}nRT = \frac{3}{2}Nk_B T \quad \Rightarrow \quad \left(\frac{\partial T}{\partial V} \right)_U = 0,$$

so that

$$\Rightarrow T_2 = T_1,$$

which means that for the ideal gas the free expansion is an isothermal expansion, in agreement with Joule's findings.

3.4.5 Adiabatic process

An *adiabatic process* happens without heat transfer:

$$\delta Q = 0.$$

From the first law of thermodynamics it follows that

$$dU = -PdV,$$

and, since $dU = C_V dT$,

$$C_V dT + PdV = 0.$$

In the case of an ideal gas, we can use the equation of state, $PV = Nk_B T$, to express dT as

$$dT = \frac{d(PV)}{Nk_B} = \frac{PdV + VdP}{Nk_B}.$$

Then

$$C_V(PdV + VdP) + Nk_B PdV = 0,$$

$$C_V VdP + (C_V + Nk_B)PdV = 0,$$

$$C_V VdP + C_P PdV = 0,$$

or

$$\boxed{\frac{dP}{P} + \gamma \frac{dV}{V} = 0}, \quad (3.2)$$

where

$$\boxed{\gamma \equiv \frac{C_P}{C_V}}.$$

We assume that γ is a constant and, integrating eq. (3.2), obtain

$$\ln P = -\gamma \ln V + \text{const},$$

$$\boxed{PV^\gamma = \text{const}}$$

and, using the ideal gas's equation of state,

$$\boxed{TV^{\gamma-1} = \text{const}}.$$

Since $\gamma > 1$, an adiabatic path has a steeper slope than an isotherm in a $P - V$ diagram (Fig. 3.8).

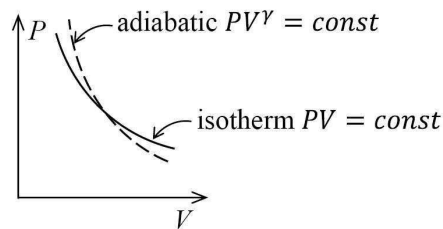


Figure 3.8: Adiabatic path versus isothermal path in a $P - V$ diagram.

3.5 Heat equations

The internal energy is a continuous differentiable function of the variables P , V , and T . Since the constraint imposed by the equation of state reduces the number of independent variables to two, we may consider the internal energy to be a function of any two of the variables. Then, under infinitesimal increments of the variables, we will have for dU :

$$dU(P, V) = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV, \quad (3.3)$$

$$dU(P, T) = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT, \quad (3.4)$$

$$dU(V, T) = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT. \quad (3.5)$$

Like in the previous sections, the heat absorbed by the system can be written in the form

$$\delta Q = dU + PdV.$$

We use now expressions (3.3), (3.4), and (3.5) to write δQ as

$$\delta Q = \left(\frac{\partial U}{\partial P}\right)_V dP + \left[\left(\frac{\partial U}{\partial V}\right)_P + P\right] dV, \quad (3.6)$$

$$\delta Q = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT + PdV, \quad (3.7)$$

$$\delta Q = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV + \left(\frac{\partial U}{\partial T}\right)_V dT. \quad (3.8)$$

We can rewrite dV as

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

and substitute this expression into eq. (3.7):

$$\delta Q = \left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP + \left(\frac{\partial(U + PV)}{\partial T}\right)_P dT.$$

We define the state function *enthalpy*

$$\boxed{H \equiv U + PV},$$

so that eq. (3.7) now reads

$$\boxed{\delta Q = \left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP + \left(\frac{\partial H}{\partial T}\right)_P dT}.$$

The heat capacities can then be expressed as derivatives of state functions:

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \text{and} \quad C_P = \left(\frac{\partial H}{\partial T}\right)_P}.$$

3.6 Magnetic systems

In the previous sections we have introduced and studied the ideal gas. In this section we will consider a magnetic system.

For a magnetic substance, the thermodynamic variables are

- \mathcal{H} : intensive magnetic field generated by external currents;
- M : extensive magnetization.

The magnetic work done on the system is

$$\delta W = \mathcal{H}dM.$$

The first law of thermodynamics then reads

$$dU = \delta Q + \mathcal{H}dM. \quad (3.9)$$

Expression (3.9) maps into that for a PVT system under the correspondence

$$\mathcal{H} \leftrightarrow -\mathcal{P},$$

$$M \leftrightarrow V.$$

In a paramagnetic substance, a magnetic field induces magnetization density given by

$$\frac{M}{V} = \chi\mathcal{H},$$

where χ is the magnetic susceptibility that obeys Curie's law:

$$\chi = \frac{c_0}{T}.$$

From that we can derive an equation of state for the magnetization

$$\boxed{M = \frac{k\mathcal{H}}{T}},$$

with $k = c_0V$.

An idealized uniform ferromagnetic system has a phase transition at a critical temperature T_c , which is not induced by an external field. Below T_c , the system becomes a *permanent magnet* (spontaneous magnetization – Fig. 3.9).

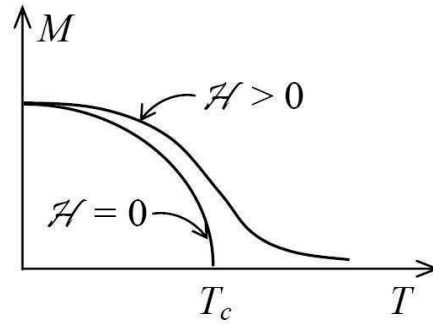


Figure 3.9: Ferromagnetic phase transition in a $M - T$ diagram. For $\mathcal{H} \neq 0$ there is no phase transition; the system always has $M \neq 0$.

A real ferromagnet is usually composed of domains (Fig. 3.10). The configuration of the domains is such as to minimize the magnetic energy by reducing the surface fields. At a fixed $T < T_C$, the domain walls move in response to the change of \mathcal{H} . This is a dissipative process that leads to hysteresis (Fig. 3.11).

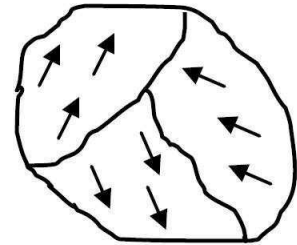


Figure 3.10: Magnetic domains.

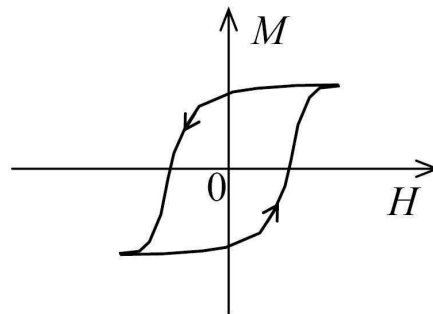


Figure 3.11: Hysteresis in a ferromagnet due to the formation of ferromagnetic domains.