# 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)

$$dV \; = \; a \, dx \; ,$$

where $a$ is the active area of the piston. In equilibrium, the external force $F$ is related to pressure $P$ as

$$F \; = \; -Pa \; .$$
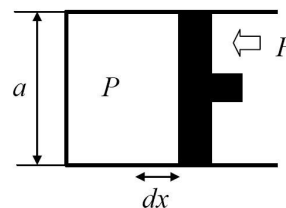
For an infinitesimal process, the change of the position of the wall by $dx$ results in performing work $\delta W$:

$$\delta W = F dx = -P dV, \qquad \delta W = -P a \, dx \; . \tag{3.1}$$

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

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

**Note**:

- Mechanical work is *positive* when it is performed *on* the system.

- $\delta W$ is not an exact differential, i.e., $W(P, V)$ does not define any state property.

- $\Delta W$ depends on the path connecting $A$ $(V_1)$ and $B$ $(V_2)$.

**Cyclic process.** During a *cyclic process* the path in the equation-of-state space is a closed loop; the work done is along a closed cycle on the equation-of-state surface $f(P, V, T) = 0$:

$$W = - \oint P dV.$$
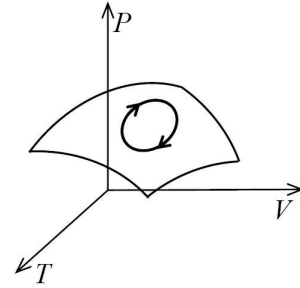
## 3.2   Heat

Energy is transferred in a system in the from of *heat* when no mechanical work is exerted, viz when $\delta W = -PdV$ vanishes. Compare (3.1). Other forms of energy (magnetic, electric, gravitational, ...) are also considered to be constant.

Heat transfer is a thermodynamic process representing the transfer of energy in the form of thermal agitation of the constituent particles. In practice one needs heating elements to do the job, f.i. a flame.

As an example of a process where only heat is transferred, we consider two isolated systems with temperatures $T_A$ and $T_B$ such that $T_A > T_B$. The two systems are brought together without moving the wall between them. Due to the 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*.
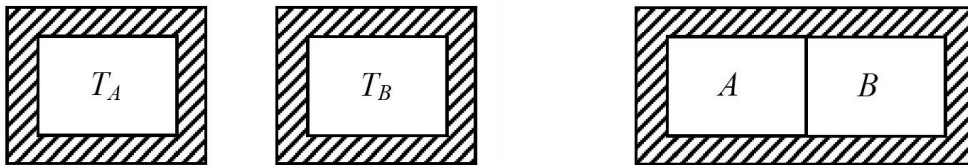
**Heat capacity.** If a system absorbs an amount of heat $\Delta Q$, its temperature rises *proportionally* by an amount $\Delta T$:

$$\boxed{\Delta Q = C \Delta T} \; . \tag{3.2}$$

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

**Specific heat.** The *intensive heat capacity c* may take various forms:

$$
\begin{array}{rcl}
\text{per particle} & : & C/N \\
\text{per mole} & : & C/n \\
\text{per unit volume} & : & C/V
\end{array}
$$

The unit of heat is *calorie* or, equivalently, *Joule*

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

**Thermodynamic processes.** Heat may be absorbed by a body retaining one of its defining variables constant. The various possible processes are:

$$
\begin{array}{rcl}
\text{isothermal} & : & T = \text{const.} \\
\text{isobaric} & : & P = \text{const.} \\
\text{isochoric} & : & V = \text{const.} \\
\text{adiabatic} & : & \Delta Q = 0 \ (\text{no heat is transferred})
\end{array}
$$

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

$C_V$ – for the heat capacity at constant volume,

$C_P$ – for the heat capacity at constant pressure.

**Thermodynamic response coefficients.** Examples of other thermodynamic coefficients measuring the linear response of the system to an external source are

$$
\text{compressibility} \quad : \quad \kappa = -\frac{1}{V}\frac{\Delta V}{\Delta P}
$$

$$
\text{the coefficient of thermal expansion} \quad : \quad \alpha = \frac{1}{V}\frac{\Delta V}{\Delta T}.
$$

**Sign convention.** We remind that the 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 Exact differentials

A function $f = f(x, y)$ of two variables has the differential

$$
df \ = \ Adx \ + \ Bdy, \qquad A = \frac{\partial f}{\partial x}, \qquad B = \frac{\partial f}{\partial y} \ .
$$

Reversely one says that $Adx + Bdy$ is an *exact differential* if

$$
\boxed{\frac{\partial A}{\partial y} = \frac{\partial B}{\partial x}} \ , \qquad \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \ .
$$

An example from classical example is the potential energy $\Phi(x, y)$. For all exact differentials $d\Phi$ the path of integration is irrelevant,

$$
\Phi(x_2, y_2) \ = \ \Phi(x_1, y_1) \ + \ \int_{(x_1, y_1)}^{(x_2, y_2)} d\Phi \ .
$$

Any path connecting $(x_1, y_1)$ to $(x_2, y_2)$ results in the same $\Phi(x_2, y_2)$.

**Stirling cycle.** Heat and work are both –not– exact differentials. This is an experimental fact which can be illustrated by any reversible cyclic process. As an example we consider here the *Stirling cycle*, which consist of four sub-processes.

(1) Isothermal expansion. The heat $Q_1$ delivered to the gas makes it expand at constant temperature.

(2) Isochoric cooling. The volume of the piston is kept constant while the gas cools down. The transferred heat and work are $Q_2$ and $W_2$.

(3) Isothermal compression. The heat $Q_3$ removed makes the gas contract at constant temperature.

(4) Isochoric heating. The volume of the piston is kept constant while is heated up. The transferred heat and work are $Q_4$ and $W_4$.
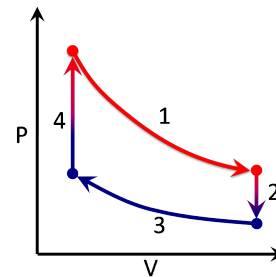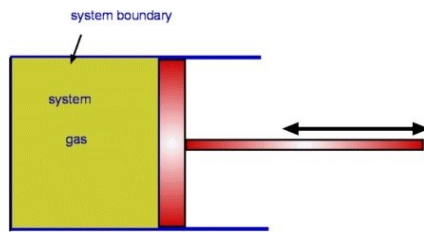


The experimental fact that the Stirling cycle can be used either as an engine ($W_2 + W_4 < 0$), or as an heat pump ($W_2 + W_4 > 0$), proves that work and heat cannot be exact differentials, viz that

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

## 3.4   First law of thermodynamics – internal energy

The first law of thermodynamics expresses that energy is conserved, when all forms of energy, including heat, are taken into account.

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

$$\Delta U \;=\; \Delta Q + \Delta W + \dots , \tag{3.3}$$

where $\Delta Q$ is heat transferred to the system and $\Delta W$ is mechanical work performed on the system. If present, other forms of energy transfer processes need to taken into account on the RHS of (3.3).

$\Delta U$ is independent of the path of transformation, although $\Delta Q$ and $\Delta W$ are path-dependent. Correspondingly, in a reversible infinitesimal transformation, the infinitesimal

$\delta Q$ and $\delta W$ are not exact differentials (in the sense that they do not represent the changes of definite functions of state), but

$$\boxed{dU \ = \ \delta Q + \delta W} \ , \qquad dU \ = \ C_V dT \ - \ P dV \tag{3.4}$$

is an exact differential. For the second part of (3.4) we have used (3.2) and (3.1), namely that $\delta Q = C_V dT$ (when the volume $V$ is constant) and that $\delta W = -P dV$.

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

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

**Statistical mechanics.** The iternal energy $U$ is a key quantity in statistical mechanics, as it is given microscopically 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 the interaction between particles (f.i. the Coulomb interaction potential between charged particles).

## 3.4.1 Internal energy of an ideal gas

We consider $N$ molecules, i.e. $n = N/N_A$ moles, in a cubic box of side $L$ and volume $V = L^3$. A particle hitting a given wall changes its momentum by

$$\Delta p_x \ = \ 2m v_x, \qquad \Delta t \ = \ 2L/v_x$$

where $m$ is the mass, $v_x$ the velocity in $x-$direction and $\Delta t$ the average time between collisions. The momentum hence changes on the average as

$$\frac{\Delta p_x}{\Delta t} \ = \ \frac{2m v_x}{2L/v_x} \ = \ \frac{m v_x^2}{L} \ = \ \frac{m \mathbf{v}^2}{3L} \ = \ \frac{2}{3L} E_{kin} \ ,$$
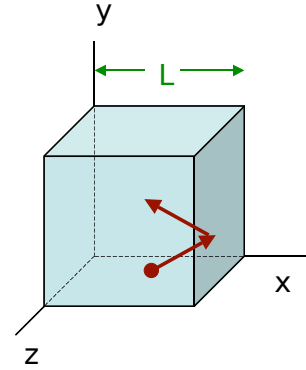
where $E_{kin} = m\mathbf{v}^2/2$ is the kinetic energy of the molecule and $\mathbf{v}^2 = v_x^2 + v_y^2 + v_z^2$.

**Newton's law.** Newton's law, $d\mathbf{p}/dt = \mathbf{F}$, tells us that the total force $F_{tot}$ on the wall is $2N E_{kin}/(3L)$. We then obtain for the pressure

$$P \ = \ \frac{F_{tot}}{L^2} \ = \ \frac{2}{3} \frac{N}{L^3} E_{kin}, \qquad E_{kin} \ = \ \frac{m}{2} \mathbf{v}^2 \ .$$

Assuming the ideal gas relation (1.3) we find consequently

$$P \ = \ \frac{N}{V} k_B T \ = \ \frac{2}{3} \frac{N}{L^3} E_{kin}, \qquad E_{kin} \ = \ \frac{3}{2} k_B T \tag{3.5}$$

for the kinetic energy $E_{kin}$ of a single molecule. The internal energy is then, with $\phi(\vec{r}_i) = V(\vec{r}_i - \vec{r}_j) = 0$,

$$\boxed{U = \frac{3}{2} Nk_B T = \frac{3}{2} nRT = \frac{3}{2} PV} \ , \tag{3.6}$$

where $R = 8.314 \,\mathrm{J/(mol\,K)}$ is the gas constant.

## 3.5 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.
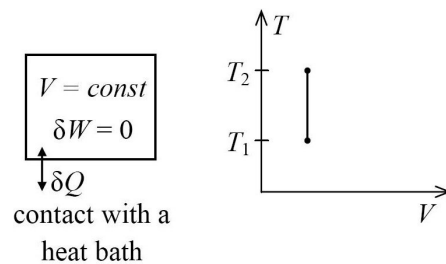
### 3.5.1 Isochoric process

An *isochoric process* is a constant volume process. We have hence

$$dV = 0, \qquad \delta W = 0, \qquad \boxed{dU|_V = \delta Q|_V} \ ,$$

and

$$\boxed{\left( \frac{\delta Q}{dT} \right)_V = \left( \frac{dU}{dT} \right)_V = C_V} \tag{3.7}$$

for the heat capacity at constant volume $C_V$.

**Ideal gas.** An ideal gas containing $n$ moles is defined by its equation of state,

$$\boxed{PV = Nk_B T} \ , \qquad Nk_B = nR \ . \tag{3.8}$$

Using the internal energy (3.6),

$$U = \frac{3}{2} Nk_B T = \frac{3}{2} nRT, \qquad dU = \frac{3}{2} nRdT \ ,$$

we obtain

$$\boxed{C_V = \frac{3}{2} nR = \frac{3}{2} \frac{PV}{T}} \tag{3.9}$$

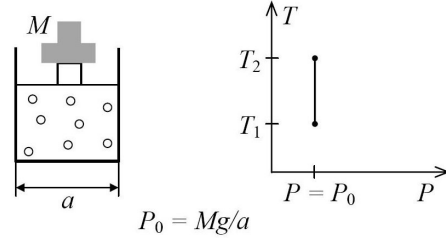for the heat capacity of the ideal gas at constant volume.

### 3.5.2 Isobaric process

An *isobaric process* is a constant pressure process. In order to evaluate $C_P$ we consider

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

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

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

The specific heat at constant pressure,

$$\boxed{C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P} , \qquad (3.10)$$

reduces then for an ideal gas, for which $U = 3nRT/2$ and $PV = nRT$, to

$$\boxed{C_P = \frac{3}{2}nR + nR = \frac{5}{2}nR = C_V + Nk_B} . \qquad (3.11)$$

**Mayer's relation between $C_P$ and $C_V$.** In order to evaluate the partial derivative $(\partial U/\partial T)_P$ entering the definition (3.10) of the specific heat at constant pressure we note that the equation of state $f(P,V,T) = 0$ determines the interrelation between $P$, $V$ and $T$. A constant pressure $P$ defines hence a functional dependence between $V$ and $T$. We therefore have

$$\left(\frac{\partial U}{\partial T}\right)_P = \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{= C_V} \underbrace{\left(\frac{\partial T}{\partial T}\right)_P}_{= 1} + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$
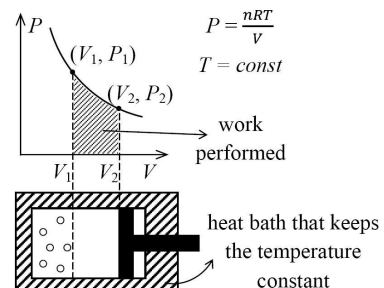
and hence with

$$C_P = C_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P \qquad (3.12)$$

the *Mayer relation*. In Sect. 4.5 we will connect the partial derivatives entering (3.12) with measurable quantities.

### 3.5.3 Isothermal processes for the ideal gas

An *isothermal process* takes place at constant temperature. The work performed

$$\Delta W = -\int_{V_1}^{V_2} dV\, P$$

is hence given by the area below $P = P(T, V)|_T$. Using
the equation-of-state relation $PV = nRT$ of the ideal
gas we obtain

$$
\begin{aligned}
\Delta W &= -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1} \\
&= -\Delta Q \ ,
\end{aligned}
$$

where the last relation follow from the first law, $\Delta U = \Delta Q + \Delta W$, and from the fact that the internal energy $U = 3nRT/2$ of the ideal gas remains constant during the isothermal process. $\Delta W > 0$ for $V_1 > V_2$, viz when the gas is compressed.

**Note.** Heat cannot be transformed in work forever, as we will discuss in the next chapter.

### 3.5.4  Free expansion of an ideal gas

A classical experiment, as performed first by Joule, consist of allowing a thermally isolated ideal gas to expand freely into an isolated chamber, which had been initially empty. After a new equilibrium state was established, in which the gas fills both compartments, the final temperature of the gas is found to be identical to the initial temperature.
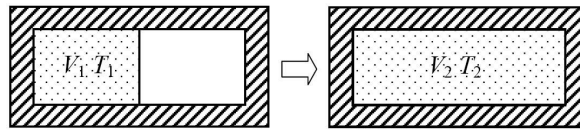


The expansion process is overall isolated. Neither heat nor work is transferred into the system,

$$
\Delta W = 0, \qquad \Delta Q = 0, \qquad \Delta U = 0 \ ,
$$

and internal energy $U$ stay constant

**Ideal gas.** The internal energy

$$
U = \frac{3}{2} nRT,
$$

of the ideal gas with a contant number $n$ of mols depends only on the temperature $T$, and not on the volume $V$. The kinetic energy $E_{kin} = 3k_B T/2$ of the constitutent particles is not contingent on the enclosing volume. We hence have

$$
\left( \frac{\partial T}{\partial V} \right)_U = 0, \qquad T_2 = T_1 \ .
$$

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

### 3.5.5 Adiabatic processes for the ideal gas

An *adiabatic process* happens without heat transfer:

$$\delta Q = 0, \qquad dU = -PdV \ ,$$

where the second relation follows from the first law of thermodynamics, $dU = \delta Q + \delta W$. For the ideal gas we have $PV = nRT$, $U = 3nRT/2 = 3PV/2$ and hence

$$dU = \frac{3}{2}\Big(PdV + VdP\Big) = -PdV, \qquad \boxed{\frac{5}{2}\frac{dV}{V} = -\frac{3}{2}\frac{dP}{P}}\ ,$$
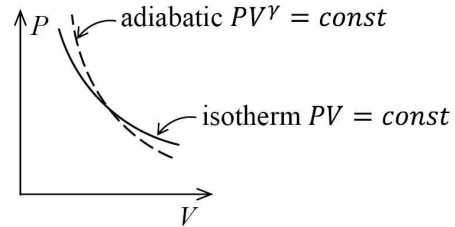
which can be solved as

$$\gamma \log\left(\frac{V}{V_0}\right) = \log\left(\frac{P_0}{P}\right), \qquad \boxed{PV^\gamma = \text{const.}}\ , \qquad \gamma = 5/3 \ .$$

Using the ideal gas equation of state, $PV = nRT$, we may write equivalently

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

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



## 3.6 Enthalpy

The internal energy is a continuous differentiable state function for which the relations

$$dU = \delta Q - PdV, \qquad \delta Q = C_V dT, \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

hold. One can define equivalently with

$$\boxed{H \equiv U + PV}\ , \tag{3.13}$$

a state function $H$, denote the *enthalpy*, which obeys

$$dH = \delta Q + VdP, \qquad \delta Q = C_P dT, \qquad C_P = \left(\frac{\partial H}{\partial T}\right)_P \ . \tag{3.14}$$

Note that $P$, $V$ and $T$ determine each others in pairs via the equation-of-state function $f(P,V,T) = 0$.

**Derivation.** We have

$$\begin{aligned} dH &= dU + PdV + VdP = \delta Q - PdV + PdV + VdP \\ &= \delta Q + VdP \ , \end{aligned}$$

in accordance with and (3.14), and

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

in agreement with the definition (3.10) of the specific heat $C_P$ at constant pressure.

## 3.7   Magnetic systems

We now discuss how the concepts developed hitherto for a mono-atomic and non-magnetic gas can be generalized to for which either a magnetization $M$ and/or a magnetic field $\mathcal{H}$ is present.

- $\mathcal{H}$: magnetic field (intensive, generated by external currents)

- $M$: magnetization (extensive, produced by ordered local moments)
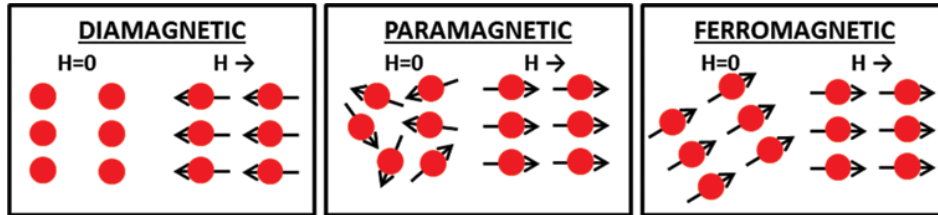


**Magnetic work.** The magnetic work done on the system is $\mathcal{H}dM$, as derived in electrodynamics. The modified first law of thermodynamics then takes the form,

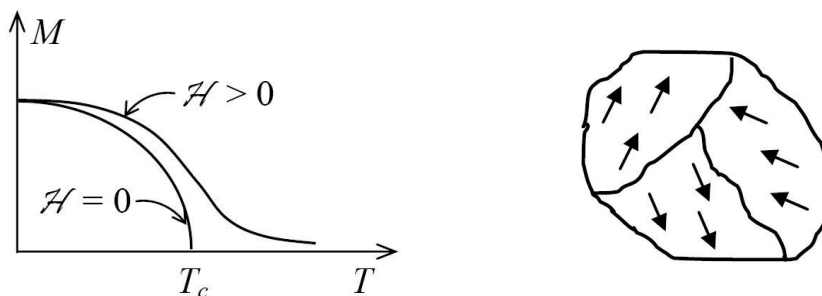$$dU = \delta Q + \delta W, \qquad \delta W = \mathcal{H}dM , \qquad (3.15)$$

when the volume $V$ is assumed to be constant. All results previously for the $PVT$ system can be written into $HMT$ variables when using

$$\mathcal{H} \leftrightarrow -P, \qquad M \leftrightarrow V .$$

**Susceptibility.** A magnetic field $\mathcal{H}$ induces in general a magnetization density $M/V$, which is given for a paramagnetic substance by Curie's law

$$\boxed{\frac{M}{V} = \chi(T)\,\mathcal{H}} , \qquad \chi(t) = \frac{c_0}{T} .$$

$\chi = \chi(T)$ is denoted the *magnetic susceptibility.*



**Phase transitions.** Ferromagnetic systems order spontaneously below the Curie temperature $T_c$, becoming such a *permanent magnet* with a finite magnetization $M$. The phase transition is washed-out for any finite field $\mathcal{H} \neq 0$, which induces a finite magnetization at all temperatures.

**Hysteresis.**

Impurities and lattice imperfections induce magnetic domains, which are then stabilized by minimizing the magnetic energy of the surface fields. The resulting domain walls may move in response to the change of $\mathcal{H}$. This is a dissipative process which leads to hysteresis.