Foundations of thermodynamics

Fundamental thermodynamical concepts

System is the macrophysical entity under consideration.

Surrounding is the world outside of the system.

Open system can exchange matter and heat with the surrounding.

Closed system can exchange heat with the surrounding while keeping the number of particles constant.

Isolated system can exchange neither matter nor heat with the surrounding.

Thermodynamical equilibrium

- No macroscopical changes.
- Uniquely described by external variables of state.
- System forgets its past; no hysteresis.
- *In global equilibrium* all parts of the system are in the same state.

Nonequilibrium

- For example, isolated systems each in an equilibrium state.
- *In a local thermodynamical equilibrium* semimicroscopical regions are in an equilibrium, neighbour regions in different equilibria ⇒ particles, heat ... will flow.
- From stronger nonequilibria the system usually *relaxes* to a local equilibrium.

Degree of freedom is the number of quantities needed for the exact description of the microscopic state ($\propto$ number of particles).

State variables are parameters characterizing the macroscopic state.

Extensive variable is proportional to the quantity of the substance; e.g. volume V, particle number N, internal energy U, entropy S, total magnetic moment $\int d^3r\,\boldsymbol{M}$.

Intensive variable is independent on the quantity of the substance and can be determined for every semimicroscopical volume element ΔV; e.g. temperature T, pressure p, chemical potential μ, magnetic field $\boldsymbol{H}$, ratios of extensive varialbles like $\rho = N/V$, $s = S/N, \ldots$.

Conjugated variables A and B appear in pairs in expressions for the differential of the energy, i.e. in forms $\pm A\,dB$ or $\pm B\,dA$; the one is always extensive and the other intensive.

Process is a change in the state.

Reversibel process advances via states infinitesimally close to equilibrium, *quasistatically.* The direction of a reversible process can be reversed by infinitesimal changes of external variables.

Isothermic process : T constant.

Isobaric process : p constant.

Isochoric process : V constant.

Isentropic or *adiabatic process*: S constant.

Irreversibel process is a sudden or spontaneous change during which the system is far from equilibria. In the intermediate steps global state variables (p, T, ...) are not usually defined.

Cyclic process consists of cycles which take the system every time to its initial state.

State variables and exact differentials

Let us suppose that, for example, T, V ja N tell uniquely the state of the system. State variables are then their unique functions:

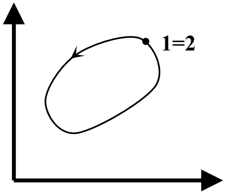
$$\begin{aligned} p &= p(T,V,N) \\ U &= U(T,V,N) \\ S &= S(T,V,N). \end{aligned}$$

In an infinitesimal change state variables transform like

$$dp = \left(\frac{\partial p}{\partial T}\right)_{V,N} dT + \left(\frac{\partial p}{\partial V}\right)_{T,N} dV + \left(\frac{\partial p}{\partial N}\right)_{T,V} dN$$

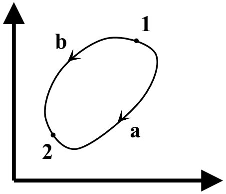
$$\vdots$$

The differentials of unique functions, dp, dT, dV, ..., are *exact differentials*: their total change evaluated over a closed path vanishes:



$$\oint_{1\to 2} dp = \oint_{1\to 2} dU = \cdots = 0.$$

The total change of an exact differential is independent on the path of integration.



$$\int_a dU - \int_b dU = 0,$$

so

$$U(2) = U(1) + \int_1^2 dU.$$

Let us denote by $\text{đ}F$ a differential which is not necessarily exact. The differential

$$\text{đ}F = F_1(x,y)\,dx + F_2(x,y)\,dy$$

is exact if
$$\frac{\partial F_1}{\partial y} = \frac{\partial F_2}{\partial x}.$$
Then $\exists F(x,y)$ so that $F_1(x,y) = \frac{\partial F(x,y)}{\partial x}$ and $F_2(x,y) = \frac{\partial F(x,y)}{\partial y}$ and
$$\int_1^2 \text{đ}F = F(2) - F(1)$$
is independent on the path. We say that $\text{đ}F = dF$ is *integrable.*

If $\text{đ}F = F_1 dx + F_2 dy$ is not exact, there exists an *integrating factor* $\lambda(x,y)$ so that in the neighbourhood of the point (x,y)
$$\lambda \text{đ}F = \lambda F_1 dx + \lambda F_2 dy = df$$
is an exact differential.

Legendre transformations can be used to make changes in the set of the indepependent state variables. For example, let us look at the function $f(x,y)$ of two variables. We denote
$$z = f_y = \frac{\partial f(x,y)}{\partial y}$$
and define the function
$$g = f - y f_y = f - yz.$$
Now
$$\begin{aligned} dg &= df - y\,dz - z\,dy = f_x dx + f_y dy - y\,dz - z\,dy \\ &= f_x dx - y\,dz. \end{aligned}$$
Thus we can take x and z as independent variables of the function g, i.e. $g = g(x,z)$. Obviously
$$y = -\frac{\partial g(x,z)}{\partial z}.$$
Corresponding to the Legendre transformation $f \to g$ there is the inverse transformation $g \to f$
$$f = g - z g_z = g + yz.$$

Often needed identities

Let $F = F(x,y)$, $x = x(y,z)$, $y = y(x,z)$ and $z = z(x,y)$. Then
$$\begin{aligned} \left(\frac{\partial F}{\partial x}\right)_z &= \left(\frac{\partial F}{\partial x}\right)_y + \left(\frac{\partial F}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \\ -1 &= \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y \\ \left(\frac{\partial x}{\partial y}\right)_z &= \frac{\left(\frac{\partial F}{\partial y}\right)_z}{\left(\frac{\partial F}{\partial x}\right)_z}. \end{aligned}$$

Equations of state

State variables of an *equilibrium* system are related by a state equation which, in most cases, is a relation between thermal variables (T or S) and mechanical variables.

Examples:

Classical ideal gas

$$\begin{aligned} pV &= Nk_BT \\ N &= \text{number of molecules} \\ k_B &= 1.3807 \cdot 10^{-23}\text{J/K} = \text{Boltzmann constant.} \end{aligned}$$

Chemists use often the form
$$\begin{aligned} pV &= nRT \\ n &= N/N_0 = \text{number of moles} \\ R &= k_B N_0 = 8.315\text{J/K mol} \\ &= \text{gas constant} \\ N_0 &= 6.0221 \cdot 10^{23} = \text{Avogadro's number.} \end{aligned}$$

If the gas is composed of m different species of molecules the equation of state is still
$$pV = Nk_BT,$$
where now
$$N = \sum_{i=1}^{m} N_i$$
and
$$p = \sum_i p_i.$$
Here
$$p_i = N_i k_B T/V$$
is the *partial pressure* of the i:th gas.

Virial expansion of real gases

$$p = k_BT\left[\rho + \rho^2 B_2(T) + \rho^3 B_3(T) + \cdots\right],$$
where
$$\rho = N/V = \text{particle density}$$
and B_n is the n:th *virial coefficient.*

Van der Waals equation

The molecules of real gases interact

- repulsively at short distances; every particle needs at least the volume $b \Rightarrow V \gtrsim Nb$.
- attractively at large distances due to the induced dipole momenta. The pressure decreases when two particles are separated by the attraction distance. The probability of this is $\propto (N/V)^2$.

We improve the ideal gas state equation
$$p'V' = Nk_BT$$
so that
$$\begin{aligned} V' &= V - Nb \\ p &= p' - a\rho^2 = \text{true pressure.} \end{aligned}$$
then
$$(p + a\rho^2)(V - Nb) = Nk_BT.$$

Solid substances

The thermal expansion coefficient

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N}$$

and the isothermal *compressibility*

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N}$$

of solid materials are very small, so the Taylor series

$$V = V_0(1 + \alpha_p T - \kappa_T p)$$

is a good approximation.

Typically

$$\begin{array}{lcl} \kappa_T & \approx & 10^{-10}/\mathrm{Pa} \\ \alpha_p & \approx & 10^{-4}/\mathrm{K}. \end{array}$$

Stretched wire

Tension $[\mathrm{N/m^2}]$

$$\sigma = E(t)(L - L_0)/L_0,$$

where L_0 is the length of the wire when $\sigma = 0$ and $E(t)$ is the temperature dependent elasticity coefficient.

Surface tension

$$\begin{array}{rcl} \sigma & = & \sigma_0\left(1 - \frac{t}{t'}\right)^n \\ t & = & \text{temperature } {}^\circ\mathrm{C} \\ t' \text{ and } n & & \text{experimental constants,} \\ & & 1 \lesssim n \lesssim 2 \\ \sigma_0 & = & \text{surface tension when } t = 0^\circ\mathrm{C}. \end{array}$$

Electric polarization

When a piece of material is in an external electric field $\boldsymbol{E}$, we define

$$\boldsymbol{D} = \epsilon_0 \boldsymbol{E} + \boldsymbol{P},$$

where

$$\begin{array}{rcl} \boldsymbol{P} & = & \text{electric polarization} \\ & = & \text{atomic total dipole momentum/volume} \\ \boldsymbol{D} & = & \text{electric flux density} \\ \epsilon_0 & = & 8.8542 \cdot 10^{-12}\mathrm{As/Vm} \\ & = & \text{vacuum permeability.} \end{array}$$

In homogenous dielectric material one has

$$\boldsymbol{P} = \left(a + \frac{b}{T}\right)\boldsymbol{E},$$

where a and b are almost constant and $a, b \geq 0$.

Curie's law

When a piece of paramagnetic material is in magnetic field $\boldsymbol{H}$ we write

$$\boldsymbol{B} = \mu_0(\boldsymbol{H} + \boldsymbol{M}),$$

where

$$\begin{array}{rcl} \boldsymbol{M} & = & \text{magnetic polarization} \\ & = & \text{atomic total magnetic moment/volume} \\ \boldsymbol{B} & = & \text{magnetic flux density} \\ \mu_0 & = & 4\pi \cdot 10^{-7}\mathrm{Vs/Am} = \text{vacuum permeability.} \end{array}$$

Polarization obeys roughly *Curie's* law

$$\boldsymbol{M} = \frac{\rho C}{T}\boldsymbol{H},$$

where ρ is the number density of paramagnetic atoms and C an experimental constant related to the individual atom.

Note Use as a thermometer: measure the quantity M/H.

0th law

If each of two bodies is separately in thermal equilibrium with a third body then they are also in thermal equilibrium with each other ⇒ there exists a property called *temperature* and *thermometer* which can be used to measure it.

Work

Work is exchange of such "noble" energy that can be completely transformed to some other noble form of energy; e.g. mechanical and electromagnetic energy.

Sign convention: work ΔW is *the work done by the system to its surrounding.*

Example pVT system

$$\Delta W = p\,\Delta V.$$

Note $\text{đ}W$ is *not* an exact differential. Instead

$$\frac{1}{p}\text{đ}W = dV$$

is exact, i.e, $1/p$ is the integrating factor for work.

Example

$$\text{đ}W = p\,dV - \sigma A\,dL - \boldsymbol{E}\cdot d\boldsymbol{P} - \boldsymbol{H}\cdot d\boldsymbol{M}.$$

In general

$$\text{đ}W = \sum_i f_i dX_i = \boldsymbol{f}\cdot d\boldsymbol{X},$$

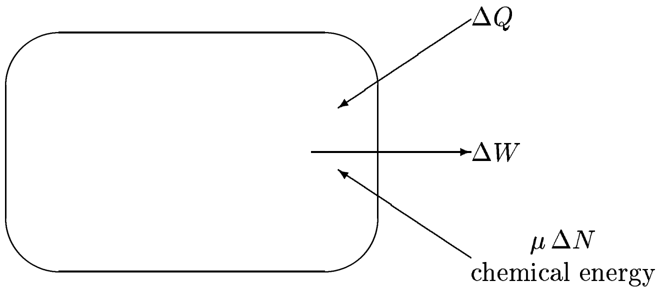
where f_i is a component of a *generalized force* and X_i a component of a *generalized displacement.*

1st law

In addition to work a system can exchange *chemical energy*, i.e. *heat* with its surroundings. Thermal energy is related to the energy of the thermal stochastic motion of microscopic particles.

The total energy of a body is called *internal energy.*

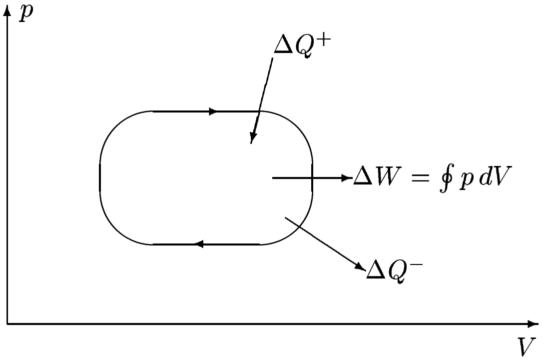
Sign conventions:



Due to the energy conservation law the change of the internal energy satisfies

$$dU = \text{đ}Q - \boldsymbol{f}\cdot d\boldsymbol{X} + \sum_i \mu_i dN_i.$$

U is a state variable, i.e. dU is exact.
In a cyclic process $\oint dU = 0$, so $\Delta W = \Delta Q$ (no change in chemical energy). In a pVT-system



The total change of heat is

$$\Delta Q = \Delta Q^+ + \Delta Q^-,$$

where ΔQ^+ is the heat taken by the system and ΔQ^- the heat released by the system.
The *efficiency* η is

$$\eta = \frac{\Delta W}{\Delta Q^+} = \frac{\Delta Q^+ + \Delta Q^-}{\Delta Q^+} = 1 - \frac{|\Delta Q^-|}{|\Delta Q^+|}.$$

2nd law

(a) Heat cannot be transferred from a cooler heat reservoir to a warmer reservoir without any other consequences.

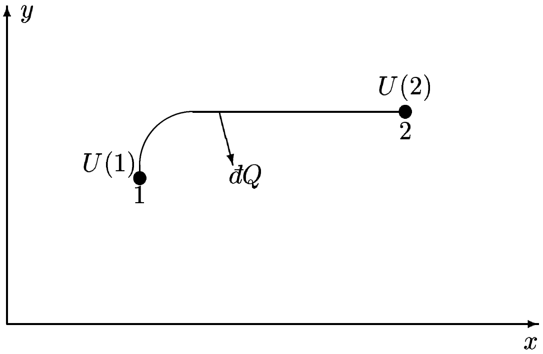
(b) In a cyclic process it is not possible to convert all heat taken from the hotter heat reservoir to work.

(c) It is not possible to reverse the evolution of a system towards thermodynamical equilibrium without converting work to heat.

(d) The change of the total entropy of the system and its surroundings is positive and can be zero only in reversible processes.

(e) Of all the engines working between the temperatures T_1 and T_2 the Carnot engine has the highest efficiency.

We consider the infinitesimal process



Now

$$\text{đ}Q = dU + \text{đ}W = dU + \boldsymbol{f}\cdot d\boldsymbol{X},$$

so there exists an integrating factor $1/T$ so that

$$\frac{1}{T}\text{đ}Q = dS$$

is exact. The state variable S is *entropy* and T turns out to be the so called *absolute* temperature.
The second law (d) can now be written as

$$\frac{dS_{\text{tot}}}{dt} \geq 0.$$

In an isolated system we have

$$dS \geq \frac{1}{T}\text{đ}Q,$$

where the equality holds only for reversible processes.
For reversible processes the first law can be rewritten as

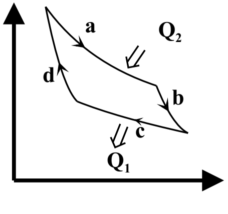
$$dU = \text{đ}Q - \text{đ}W + \mu\,dN = T\,dS - p\,dV + \mu\,dN.$$

Carnot's cycle

The Carnot cycle $\mathcal{C}$ consists of reversible processes

a)	isothermic	T_2	$\Delta Q_2 > 0$
b)	adiabatic	$T_2 \to T_1$	$\Delta Q = 0$
c)	isothermic	T_1	$\Delta Q_1 > 0$
d)	adiabatic	$T_1 \to T_2$	$\Delta Q = 0$

Now $\Delta U = 0$, so $\Delta W = \Delta Q_2 - \Delta Q_1$.



We define the efficiency as

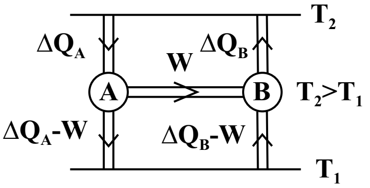
$$\eta = \frac{\Delta W}{\Delta Q_2} = 1 - \frac{\Delta Q_1}{\Delta Q_2}.$$

Because the processes are reversible the cycle $\mathcal{C}$ can be reversed and $\mathcal{C}$ works as a heat pump.
Let us consider two Carnot cycles $\mathcal{A}$ and $\mathcal{B}$, for which

$$\Delta W_{\mathcal{A}} = \Delta W_{\mathcal{B}} = \Delta W.$$

$\mathcal{A}$ is an enegine and $\mathcal{B}$ a heat pump. The efficiences are correspondingly

$$\eta_{\mathcal{A}} = \frac{\Delta W}{\Delta Q_{\mathcal{A}}} \text{ and } \eta_{\mathcal{B}} = \frac{\Delta W}{\Delta Q_{\mathcal{B}}}.$$



Let us suppose that

$$\eta_{\mathcal{A}} > \eta_{\mathcal{B}},$$

so that $\Delta Q_{\mathcal{B}} > \Delta Q_{\mathcal{A}}$ or $\Delta Q_{\mathcal{B}} - \Delta Q_{\mathcal{A}} > 0$. The heat would transfer from the cooler reservoir to the warmer one without any other changes, which is in contradiction with the second law (form a). So we must have

$$\eta_{\mathcal{A}} \le \eta_{\mathcal{B}}.$$

Similarly one can show that

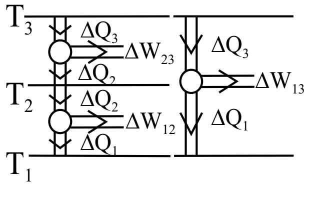
$$\eta_{\mathcal{B}} \le \eta_{\mathcal{A}},$$

so that $\eta_{\mathcal{A}} = \eta_{\mathcal{B}}$, i.e. all Carnot engines have the same efficiency.
Note The efficiency does not depend on the realization of the cycle (e.g. the working substance) ⇒ The efficiency depends only on the temperatures of the heat reservoirs.
Similarly, one can show that the Carnot engine has the highest efficiency among all engines (also irreversible) working between given temperatures.
Let us consider Carnot's cycle between temperatures T_3 and T_1. Now

$$\eta = 1 - f(T_3, T_1),$$

where

$$f(T_3, T_1) = \frac{\Delta Q_1}{\Delta Q_3}.$$



Here

$$\begin{aligned} f(T_3, T_2) &= \frac{\Delta Q_2}{\Delta Q_3} \\ f(T_2, T_1) &= \frac{\Delta Q_1}{\Delta Q_2} \\ f(T_3, T_1) &= \frac{\Delta Q_1}{\Delta Q_3} \end{aligned}$$

so

$$f(T_3, T_1) = f(T_3, T_2) f(T_2, T_1).$$

The simplest solution is

$$f(T_2, T_1) = \frac{T_1}{T_2}.$$

We define the *absolute temperature* so that

$$\eta = 1 - \frac{T_1}{T_2}.$$

The Carnot cycle satisfies

$$\oint \frac{\text{đ}Q}{T} = 0,$$

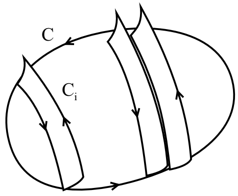
since

$$\int_a \frac{\text{đ}Q}{T} = \frac{\Delta Q_2}{T_2}$$

and

$$\int_c \frac{\text{đ}Q}{T} = -\frac{\Delta Q_1}{T_1} = -\frac{\Delta Q_2}{T_2}.$$

This is valid also for an arbitrary reversible cycle



because

$$\oint_C \frac{\text{đ}Q}{T} = \sum_i \oint_{C_i} \frac{\text{đ}Q}{T} = 0.$$

So

$$dS = \frac{\text{đ}Q}{T}$$

is exact and the *entropy* S is a state variable.
Because the Carnot cycle has the highest efficiency a cycle containing irreversible processes satisfies

$$\eta_{\text{irr}} = 1 - \frac{\Delta Q_1}{\Delta Q_2} < \eta_{\text{Carnot}} = 1 - \frac{T_1}{T_2}$$

or

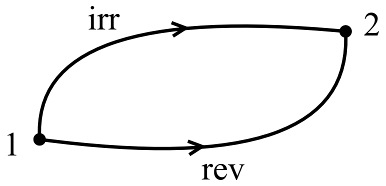
$$\frac{\Delta Q_2}{T_2} - \frac{\Delta Q_1}{T_1} < 0.$$

Thus for an arbitrary cycle we have

$$\oint \frac{\text{đ}Q}{T} \le 0, \qquad (*)$$

where the equality holds only for reversible processes.
For an arbitrary process 1 → 2 the change of the entropy can be obtained from the formula

$$\Delta S = \int_{\text{rev}} dS = \int_{\text{rev}} \frac{\text{đ}Q}{T}.$$



According to the formula $(*)$ we have

$$\int_{\text{irr}} \frac{đQ}{T} - \int_{\text{rev}} \frac{đQ}{T} < 0,$$

or

$$\Delta S > \int_{\text{irr}} \frac{đQ}{T}.$$

This is usually written as

$$dS \geq \frac{đQ}{T}$$

and the equality is valid only for reversible processes.
In an isolated system we have

$$\Delta S \geq 0.$$

3rd law

Nernst's law:

$$\lim_{T \to 0} S = 0.$$

A less strong form can be stated as:
When the maximum heat occuring in the process from a state a to a state b approaches zero the also the entropy change $\Delta S_{a \to b} \to 0$.
Note There are systems whose entropy at low temperatures is larger than true equilibria would allow.