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, magnetization $\boldsymbol{M} = \int \mathrm{d}\boldsymbol{r}\, \boldsymbol{m}$, where $\boldsymbol{m}$ is magnetic moment/volume.

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 $\pm A\, \mathrm{d}B$ or $\pm B\, \mathrm{d}A$; 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

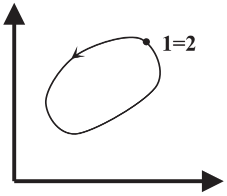
Let us suppose that, for example, T, V ja N tell uniquely the state of the system. State variables are then their unique functions:

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

In an infinitesimal change state variables transform like

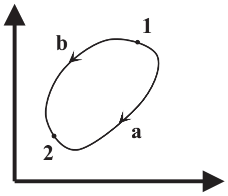
$$\begin{aligned} \mathrm{d}p &= \left(\frac{\partial p}{\partial T}\right)_{V,N} \mathrm{d}T + \left(\frac{\partial p}{\partial V}\right)_{T,N} \mathrm{d}V + \left(\frac{\partial p}{\partial N}\right)_{T,V} \mathrm{d}N \\ &\vdots \end{aligned}$$

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



$$\oint_{1\to 2} \mathrm{d}p = \oint_{1\to 2} \mathrm{d}U = \cdots = 0.$$

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



$$\int_a \mathrm{d}U - \int_b \mathrm{d}U = 0,$$

so

$$U(2) = U(1) + \int_1^2 \mathrm{d}U.$$

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

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

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 $\text{đ}F = \mathrm{d}F$ is *integrable.*

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

$$\lambda\text{đ}F = \lambda F_1\mathrm{d}x + \lambda F_2\mathrm{d}y = \mathrm{d}f$$

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

$$g = f - yf_y = f - yz.$$

Now

$$\begin{aligned} \mathrm{d}g &= \mathrm{d}f - y\,\mathrm{d}z - z\,\mathrm{d}y = f_x\mathrm{d}x + f_y\mathrm{d}y - y\,\mathrm{d}z - z\,\mathrm{d}y \\ &= f_x\mathrm{d}x - y\,\mathrm{d}z. \end{aligned}$$

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 $g \to f$

$$f = g - zg_z = g + yz.$$

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

$$\begin{aligned} pV &= nRT \\ n &= N/N_0 = \text{number of moles} \\ R &= k_BN_0 = 8.315\text{J/K mol} \\ &= \text{gas constant} \\ N_0 &= 6.0221 \cdot 10^{23} = \text{Avogadro's number.} \end{aligned}$$

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

$$p_i = N_ik_BT/V$$

is the *partial pressure* of the i:th gas.

Virial expansion of real gases

$$p = k_BT\left[\rho + \rho^2B_2(T) + \rho^3B_3(T) + \cdots\right],$$

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

$$\begin{aligned} \kappa_T &\approx 10^{-10}/\text{Pa} \\ \alpha_p &\approx 10^{-4}/\text{K}. \end{aligned}$$

Stretched wire

Tension [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

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

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

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

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

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

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 $\Rightarrow$ 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

$$\frac{1}{p}\text{đ}W = \mathrm{d}V$$

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

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

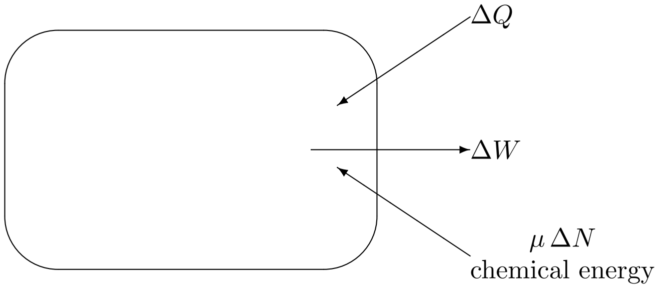
In general

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

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

1st law

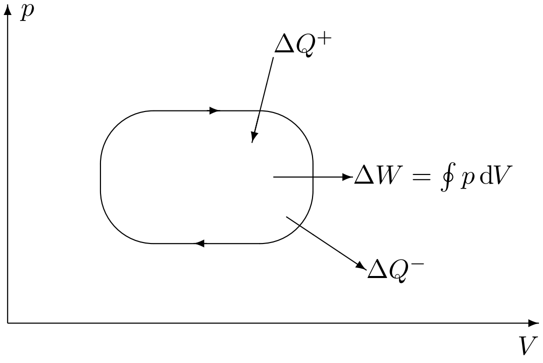
In addition to work a system can exchange *thermal energy*, i.e. *heat* with its surroundings. Thermal energy is related to the energy of the thermal stochastic motion of microscopic particles.
The total energy of a body is called *internal energy*.
Sign conventions:



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

$$\mathrm{d}U = \text{đ}Q - \boldsymbol{f}\cdot\mathrm{d}\boldsymbol{X} + \sum_i \mu_i \mathrm{d}N_i.$$

U is a state variable, i.e. $\mathrm{d}U$ is exact.
In a cyclic process $\oint \mathrm{d}U = 0$, 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.

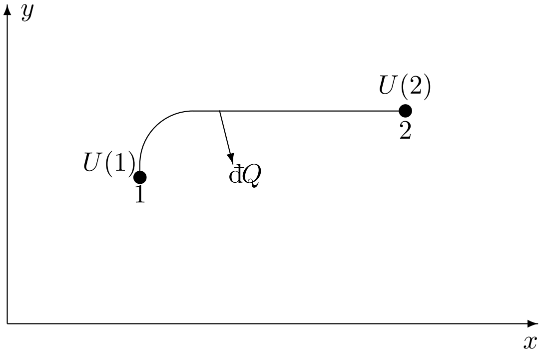
(b) In a cyclic process it is not possible to convert all heat taken from the hotter heat reservoir to work.

(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

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

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

$$\frac{1}{T}\text{đ}Q = \mathrm{d}S$$

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

$$\frac{\mathrm{d}S_{\mathrm{tot}}}{\mathrm{d}t} \geq 0.$$

For arbitrary processes we have

$$\mathrm{d}S \geq \frac{1}{T}đQ,$$

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

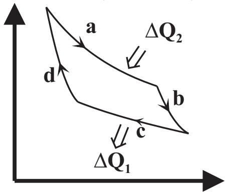
$$\mathrm{d}U = đQ - đW + \mu\,\mathrm{d}N = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N.$$

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

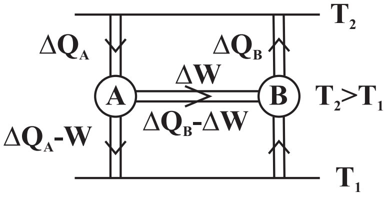
$$\eta = \frac{\Delta W}{\Delta Q_2} = 1 - \frac{\Delta Q_1}{\Delta Q_2}.$$

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 engine 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

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

Similarly one can show that

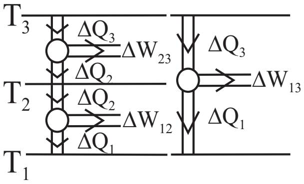
$$\eta_{\mathcal{B}} \leq \eta_{\mathcal{A}},$$

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

$$\oint \frac{đQ}{T} = 0,$$

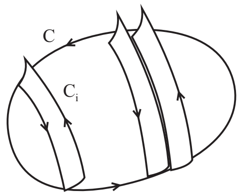
since

$$\int_a \frac{đQ}{T} = \frac{\Delta Q_2}{T_2}$$

and

$$\int_c \frac{đQ}{T} = -\frac{\Delta Q_1}{T_1} = -\frac{\Delta Q_2}{T_2}.$$

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

$$\mathrm{d}S = \frac{\text{đ}Q}{T}$$

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

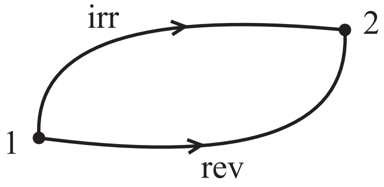
$$\frac{\Delta Q_2}{T_2} - \frac{\Delta Q_1}{T_1} < 0.$$

Thus for an arbitrary cycle we have

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

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

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



According to the formula $(*)$ we have

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

or

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

This is usually written as

$$\mathrm{d}S \geq \frac{\text{đ}Q}{T}$$

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 then 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.

Thermodynamic potentials

Fundamental equation

According to the first law

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N \tag*{($*$)}$$

S, V and N are the natural variables of the internal energy U, i.e.

$$U = U(S, V, N).$$

Furthermore, from the law ($*$) one can read the relations

$$\begin{aligned}\left(\frac{\partial U}{\partial S}\right)_{V,N} &= T\\ \left(\frac{\partial U}{\partial V}\right)_{S,N} &= -p\\ \left(\frac{\partial U}{\partial N}\right)_{S,V} &= \mu.\end{aligned} \tag*{($**$)}$$

Now U, S, V and N are extensive so we have

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)\ \forall\lambda. \tag*{($***$)}$$

Let $S \to S + \epsilon S$, $V \to V + \epsilon V$ and $N \to N + \epsilon N$, when ϵ is infinitesimal. Then

$$U(S+\epsilon S, V+\epsilon V, n+\epsilon N) = U(S, V, N) + \left(\frac{\partial U}{\partial S}\right)_{V,N}\epsilon S + \left(\frac{\partial U}{\partial V}\right)_{S,N}\epsilon V + \left(\frac{\partial U}{\partial N}\right)_{S,V}\epsilon N.$$

On the other hand, according to the equation ($***$) we have

$$U(S+\epsilon S, V+\epsilon V, N+\epsilon N) = U(S, V, N) + \epsilon U(S, V, N).$$

We end up with the *Euler equation for homogenous functions*

$$U = S\left(\frac{\partial U}{\partial S}\right)_{V,N} + V\left(\frac{\partial U}{\partial V}\right)_{S,N} + N\left(\frac{\partial U}{\partial N}\right)_{S,V}.$$

Substituting the partial derivatives ($**$) this takes the form

$$U = TS - pV + \mu N$$

or

$$S = \frac{1}{T}(U + pV - \mu N).$$

This is called the *fundamental equation.*

Internal energy and Maxwell relations

Because

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$$

and

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,N},$$

so

$$\frac{\partial T}{\partial V} = \frac{\partial}{\partial V}\frac{\partial U}{\partial S} = \frac{\partial}{\partial S}\frac{\partial U}{\partial V} = -\frac{\partial p}{\partial S}.$$

Similar relations can be derived also for other partial derivatives of U and we get so called *Maxwell's relations*

$$\begin{aligned}\left(\frac{\partial T}{\partial V}\right)_{S,N} &= -\left(\frac{\partial p}{\partial S}\right)_{V,N}\\ \left(\frac{\partial T}{\partial N}\right)_{S,V} &= \left(\frac{\partial \mu}{\partial S}\right)_{V,N}\\ \left(\frac{\partial p}{\partial N}\right)_{S,V} &= -\left(\frac{\partial \mu}{\partial V}\right)_{S,N}.\end{aligned}$$

In an irreversible process

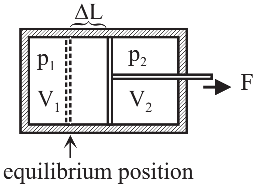
$$T\,\Delta S > \Delta Q = \Delta U + \Delta W,$$

so

$$\Delta U < T\,\Delta S - p\,\Delta V + \mu\,\Delta N.$$

If S, V and N stay constant in the process then the internal energy decreases. Thus we can deduce that *In an equilibrium with given S, V and N the internal energy is at the minimum.*

We consider a reversible process in an isolated system



We partition ΔW into the components

$$\begin{aligned}\int p\,\mathrm{d}V &= \left[\begin{array}{l}\text{work due to the}\\ \text{change of the}\\ \text{volume}\end{array}\right]\\ \Delta W_{\text{free}} &= \left[\begin{array}{l}\text{work done by the}\\ \text{gas against the}\\ \text{force } \boldsymbol{F}\end{array}\right].\end{aligned}$$

Now

$$\begin{aligned}\Delta W_{\text{free}} &= \Delta W_1 + \Delta W_2 = p_1\Delta V_1 + p_2\Delta V_2\\ &= (p_1 - p_2)\Delta V_1 = (p_1 - p_2)A\,\Delta L\\ &= -F\,\Delta L.\end{aligned}$$

According to the first law we have

$$\begin{aligned}\Delta U &= \Delta Q - \Delta W = \Delta Q - \int p\,\mathrm{d}V - \Delta W_{\text{free}}\\ &= \Delta Q - \Delta W_{\text{free}}.\end{aligned}$$

Because now $\Delta Q = 0$, we have

$$\Delta U = -\Delta W_{\text{free}} = F\,\Delta L,$$

i.e. when the variables S, V and N are kept constant the change of the internal energy is completely exhangeable with the work. ΔU is then called *free energy* and U *thermodynamic potential*.

Note If there are irreversible processes in an isolated system (V and N constants) then

$$\Delta W_{\text{free}} \leq -\Delta U.$$

Enthalpy

Using the Legendre transform

$$U \to H = U - V \left(\frac{\partial U}{\partial V}\right)_{S,N} = U + pV$$

We move from the variables (S, V, N) to the variables (S, p, N). The quantity

$$H = U + pV$$

is called *enthalpy*.

Now

$$\begin{aligned} \mathrm{d}H &= \mathrm{d}U + p\,\mathrm{d}V + V\,\mathrm{d}p \\ &= T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N + p\,\mathrm{d}V + V\,\mathrm{d}p \end{aligned}$$

or

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \mu\,\mathrm{d}N.$$

From this we can read the partial derivatives

$$\begin{aligned} T &= \left(\frac{\partial H}{\partial S}\right)_{p,N} \\ V &= \left(\frac{\partial H}{\partial p}\right)_{S,N} \\ \mu &= \left(\frac{\partial H}{\partial N}\right)_{S,V}. \end{aligned}$$

Corresponding Maxwell relations are

$$\begin{aligned} \left(\frac{\partial T}{\partial p}\right)_{S,N} &= \left(\frac{\partial V}{\partial S}\right)_{p,N} \\ \left(\frac{\partial T}{\partial N}\right)_{S,p} &= \left(\frac{\partial \mu}{\partial S}\right)_{p,N} \\ \left(\frac{\partial V}{\partial N}\right)_{S,p} &= \left(\frac{\partial \mu}{\partial p}\right)_{S,N}. \end{aligned}$$

In an irreversible process one has

$$\Delta Q = \Delta U + \Delta W - \mu\,\Delta N < T\,\Delta S.$$

Now $\Delta U = \Delta(H - pV)$, so that

$$\Delta H < T\,\Delta S + V\,\Delta p + \mu\,\Delta N.$$

We see that

In a process where S, p and N are constant spontaneous changes lead to the minimum of H, i.e. in an equilibrium of a (S, p, N)-system the enthalpy is at the minimum.

The enthalpy is a suitable potential for an isolated system in a *pressure bath* (p is constant).

Let us look at an isolated system in a pressure bath. Now

$$\mathrm{d}H = \mathrm{d}U + \mathrm{d}(pV)$$

and

$$\mathrm{d}U = \text{đ}Q - \text{đ}W + \mu\,\mathrm{d}N.$$

Again we partition the work into two components:

$$\text{đ}W = p\,\mathrm{d}V + \text{đ}W_{\text{free}}.$$

Now

$$\mathrm{d}H = \text{đ}Q + V\,\mathrm{d}p - \text{đ}W_{\text{free}} + \mu\,\mathrm{d}N$$

and for a finete process

$$\Delta H \leq \int T\,\mathrm{d}S + \int V\,\mathrm{d}p - \Delta W_{\text{free}} + \int \mu\,\mathrm{d}N.$$

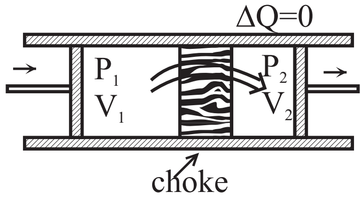
When (S, p, N) is constant one has

$$\Delta H \leq -\Delta W_{\text{free}}$$

i.e. ΔW_{free} is the minimum work required for the change ΔH.

Note An other name of enthalpy is *heat function* (in constant pressure).

Joule-Thomson phenomenon



p_1 and p_2 are temporal constants, $p_1 > p_2$ and the process irreversible. When an infinitesimal amount of matter passes through the choke the work done by the system is

$$\text{đ}W = p_2\mathrm{d}V_2 + p_1\mathrm{d}V_1.$$

	V_1	V_2
Initial state	V_{init}	0
Final state	0	V_{final}

The work done by the system is

$$\Delta W = \int \text{đ}W = p_2 V_{\text{final}} - p_1 V_{\text{init}}.$$

According to the first law we have

$$\Delta U = U_{\text{final}} - U_{\text{init}} = \Delta Q - \Delta W = -\Delta W,$$

so that

$$U_{\text{init}} + p_1 V_{\text{init}} = U_{\text{final}} + p_2 V_{\text{final}}.$$

Thus in this process the enthalpy $H = U + pV$ is constant, i.e. the process is *isenthalpic*,

$$\Delta H = H_{\text{final}} - H_{\text{init}} = 0.$$

We consider now a *reversibel* isenthalpic (and $\mathrm{d}N = 0$) process init→final. Here

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p = 0,$$

so

$$\mathrm{d}S = -\frac{V}{T}\,\mathrm{d}p. \qquad (*)$$

Now $T = T(S, p)$, so that

$$\mathrm{d}T = \left(\frac{\partial T}{\partial S}\right)_p \mathrm{d}S + \left(\frac{\partial T}{\partial p}\right)_S \mathrm{d}p.$$

On the other hand

$$\left(\frac{\partial T}{\partial S}\right)_p = \frac{T}{C_p},$$

where C_p is the isobaric heat capacity (see thermodynamical responses).
Using the Maxwell relation

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

and the partial derivative relation

$$\left(\frac{\partial V}{\partial S}\right)_p = \frac{\left(\frac{\partial T}{\partial S}\right)_p}{\left(\frac{\partial T}{\partial V}\right)_p}$$

we can write

$$\mathrm{d}T = \frac{T}{C_p}\,\mathrm{d}S + \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p.$$

Substituting into this the differential $\mathrm{d}S$ in constant enthalpy $(*)$ we get so called *Joule-Thomson coefficients*

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{T}{C_p}\left[\left(\frac{\partial V}{\partial T}\right)_p - \frac{V}{T}\right].$$

Defining the *heat expansion coefficient* α_p so that

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

we can rewrite the Joule-Thomson coefficient as

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{V}{C_p}(T\alpha_p - 1).$$

We see that when the pressure decreases the gas

- cools down, if $T\alpha_p > 1$.
- warms up, if $T\alpha_p < 1$.

For ideal gases $\left(\frac{\partial T}{\partial p}\right)_H = 0$ holds. For real gases $\left(\frac{\partial T}{\partial p}\right)_H$ is below the *inversion temperature* positive, so the gas cools down.

Free energy

The Legendre transform

$$U \to F = U - S\left(\frac{\partial U}{\partial S}\right)_{V,N}$$

or

$$F = U - TS$$

defines the (*Helmholtz*) *free energy*.
Now

$$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}N,$$

so the natural variables of F are T, V and N. We can read the partial derivateves

$$\begin{aligned} S &= -\left(\frac{\partial F}{\partial T}\right)_{V,N} \\ p &= -\left(\frac{\partial F}{\partial V}\right)_{T,N} \\ \mu &= \left(\frac{\partial F}{\partial N}\right)_{T,V}. \end{aligned}$$

From these we obtain the Maxwell relations

$$\begin{aligned} \left(\frac{\partial S}{\partial V}\right)_{T,N} &= \left(\frac{\partial p}{\partial T}\right)_{V,N} \\ \left(\frac{\partial S}{\partial N}\right)_{T,V} &= -\left(\frac{\partial \mu}{\partial T}\right)_{V,N} \\ \left(\frac{\partial p}{\partial N}\right)_{T,V} &= -\left(\frac{\partial \mu}{\partial V}\right)_{T,N}. \end{aligned}$$

In an irreversible change we have

$$\Delta F < -S\,\Delta T - p\,\Delta V + \mu\,\Delta N,$$

i.e. when the variables T, V and N are constant the system drifts to the minimum of the free energy.
Correspondingly

$$\Delta W_{\text{free}} \leq -\Delta F,$$

when (T, V, N) is constant.
Free energy is suitable for systems where the exchange of heat is allowed.

Gibbs' function

The Legendre transformation

$$U \to G = U - S\left(\frac{\partial U}{\partial S}\right)_{V,N} - V\left(\frac{\partial U}{\partial V}\right)_{S,N}$$

defines the *Gibbs function* or the *Gibbs free energy*

$$G = U - TS + pV.$$

Its differential is

$$dG = -S\,dT + V\,dp + \mu\,dN,$$

so the natural variables are T, p and N. For the partial derivatives we can read the expressions

$$\begin{aligned} S &= -\left(\frac{\partial G}{\partial T}\right)_{p,N} \\ V &= \left(\frac{\partial G}{\partial p}\right)_{T,N} \\ \mu &= \left(\frac{\partial G}{\partial N}\right)_{T,p}. \end{aligned}$$

From these we obtain the Maxwell relations

$$\begin{aligned} \left(\frac{\partial S}{\partial p}\right)_{T,N} &= -\left(\frac{\partial V}{\partial T}\right)_{p,N} \\ \left(\frac{\partial S}{\partial N}\right)_{T,p} &= -\left(\frac{\partial \mu}{\partial T}\right)_{p,N} \\ \left(\frac{\partial V}{\partial N}\right)_{T,p} &= \left(\frac{\partial \mu}{\partial p}\right)_{T,N}. \end{aligned}$$

In an irreversible process

$$\Delta G < -S\,\Delta T + V\,\Delta p + \mu\,\Delta N,$$

holds, i.e. when the variables T, p and N stay constant the system drifts to the minimum of G.
Correspondingly

$$\Delta W_{\text{free}} \le -\Delta G,$$

when (T, p, N) is constant.
The Gibbs function is suitable for systems which are allowed to exchange mechanical energy and heat.

Grand potential

The Legendre transform

$$U \to \Omega = U - S\left(\frac{\partial U}{\partial S}\right)_{V,N} - N\left(\frac{\partial U}{\partial N}\right)_{S,V}$$

defines the *grand potential*

$$\Omega = U - TS - \mu N.$$

Its differential is

$$d\Omega = -S\,dT - p\,dV - N\,d\mu,$$

so the natural variables are T, p andμ.
The partial derivatives are now

$$\begin{aligned} S &= -\left(\frac{\partial \Omega}{\partial T}\right)_{p,\mu} \\ p &= -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu} \\ N &= -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V}. \end{aligned}$$

We get the Maxwell relations

$$\begin{aligned} \left(\frac{\partial S}{\partial V}\right)_{T,\mu} &= \left(\frac{\partial p}{\partial T}\right)_{V,\mu} \\ \left(\frac{\partial S}{\partial \mu}\right)_{T,V} &= \left(\frac{\partial N}{\partial T}\right)_{V,\mu} \\ \left(\frac{\partial p}{\partial \mu}\right)_{T,V} &= \left(\frac{\partial N}{\partial V}\right)_{T,\mu}. \end{aligned}$$

In an irreversible process

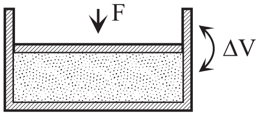
$$\Delta\Omega < -S\,\Delta T - p\,\Delta V - N\,\Delta\mu,$$

holds, i.e. when the variables T, V and μ are kept constant the system moves to the minimum of Ω.
Correspondingly

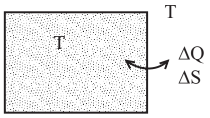
$$\Delta W_{\text{free}} \le -\Delta\Omega,$$

when (T, V, μ) is constant.
The grand potential is suitable for systems that are allowed to exchange heat and particles.

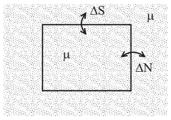
Bath
A *bath* is an equilibrium system, much larger than the system under consideration, which can exchange given extensive property with our system.
Pressure heat



The exchanged property is the volume or a corresponding generalized displacement; for example magnetization in a magnetic field.
Heat bath



Particle path



Baths can also be combined; for example a suitable potential for a pressure and heat bath is the Gibbs function G.

Thermodynamic responses

1) Volume heat expansion coefficient

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

or

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

where $\rho = N/V$.

2) Isothermic compressibility

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

3) Adiabatic compressibility

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{S,N} = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_{S,N}.$$

The velocity of sound depends on the adiabatic compressibility like

$$c_S = \sqrt{\frac{1}{m\rho\kappa_S}},$$

where m the particle mass.
One can show that

$$\kappa_T = \kappa_S + VT\,\frac{\alpha_p^2}{C_p}.$$

4) Isochoric heat capacity
In a reversible process we have

$$\Delta Q = T\,\Delta S.$$

The heat capacity C is defined so that

$$C = \frac{\Delta Q}{\Delta T} = T\,\frac{\Delta S}{\Delta T}.$$

In constant volume we define

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N}.$$

In constant volume and the number particles being fixed, according to the first law

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N = T\,\mathrm{d}S,$$

we can write

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N}.$$

5) Isobaric heat capacity

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_{p,N}$$

Because

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \mu\,\mathrm{d}N,$$

one can write

$$C_p = \left(\frac{\partial H}{\partial T}\right)_{p,N}.$$

Now

$$\begin{aligned}\left(\frac{\partial S}{\partial T}\right)_p &= \left(\frac{\partial S\left(V(p,T),T\right)}{\partial T}\right)_p \\ &= \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p\end{aligned}$$

and (a Maxwell relation)

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V,$$

so

$$C_p = C_V + T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p.$$

Since

$$\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_p\left(\frac{\partial V}{\partial p}\right)_T = -1$$

or

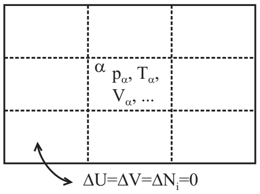
$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} = \frac{\alpha_p}{\kappa_T},$$

so

$$C_p = C_V + VT\frac{\alpha_p^2}{\kappa_T}.$$

Thermodynamic equilibrium conditions

We divide the system into fictitious semimicroscopic parts:



Extensive variables satisfy

$$\begin{aligned}S &= \sum_\alpha S_\alpha \\ V &= \sum_\alpha V_\alpha \\ U &= \sum_\alpha U_\alpha \\ N_j &= \sum_\alpha N_{j\alpha}.\end{aligned}$$

Since each element is in equlibrium the state variables are defined in each element, e.g.

$$S_\alpha = S_\alpha(U_\alpha, V_\alpha, \{N_{j\alpha}\})$$

and

$$\Delta S_\alpha = \frac{1}{T_\alpha}\,\Delta U_\alpha + \frac{p_\alpha}{T_\alpha}\,\Delta V_\alpha - \frac{\mu_{j\alpha}}{T_\alpha}\,\Delta N_{j\alpha}.$$

We suppose that the system is composed of two parts: $\alpha \in \{A, B\}$. Then

$$\Delta U_B = -\Delta U_A,\ \Delta V_B = -\Delta V_A \text{ and } \Delta N_{jB} = -\Delta N_{jA}$$

so

$$\begin{aligned}\Delta S &= \sum_\alpha \Delta S_\alpha \\ &= \left(\frac{1}{T_A}-\frac{1}{T_B}\right)\Delta U_A + \left(\frac{p_A}{T_A}-\frac{p_B}{T_B}\right)\Delta V_A \\ &\quad -\sum_j \left(\frac{\mu_{jA}}{T_A}-\frac{\mu_{jB}}{T_B}\right)\Delta N_{jA}.\end{aligned}$$

In an equilibrium S is at its maximum, so $\Delta S = 0$ and

$$\begin{aligned}T_A &= T_B \\ p_A &= p_B \\ \mu_{jA} &= \mu_{jB}.\end{aligned}$$

This is valid also when the system consists of several phases.

Stability conditions of matter

In a steady equilibrium the entropy has the true maximum so that small variations can only reduce the entropy.
We denote the equilibrium values common for all fictitious parts by the symbols T, p and $\{\mu_j\}$ and the equilibrium values of other variables by the superscript ^{0}.
We write the entropy S_α of the fictious partial system α close to an equilibrium as the Taylor series

$$\begin{aligned}&S_\alpha(U_\alpha, V_\alpha, \{N_{j\alpha}\}) = \\ &\quad S^0_\alpha(U^0_\alpha, V^0_\alpha, \{N^0_{j\alpha}\}) \\ &\quad + \left(\frac{\partial S}{\partial U_\alpha}\right)^0_{V,N}\Delta U_\alpha + \left(\frac{\partial S}{\partial V_\alpha}\right)^0_{U,N}\Delta V_\alpha \\ &\quad + \sum_j \left(\frac{\partial S}{\partial N_{j\alpha}}\right)^0_{U,V}\Delta N_{j\alpha} \\ &\quad + \frac{1}{2}\Bigg\{\Delta\left(\frac{\partial S}{\partial U_\alpha}\right)^0_{V,N}\Delta U_\alpha + \Delta\left(\frac{\partial S}{\partial V_\alpha}\right)^0_{U,N}\Delta V_\alpha \\ &\qquad + \sum_j \Delta\left(\frac{\partial S}{\partial N_{j\alpha}}\right)^0_{U,V}\Delta N_{j\alpha}\Bigg\} \\ &\quad + \cdots .\end{aligned}$$

Here $\Delta U_\alpha = U_\alpha - U^0_\alpha$ and correspondingly for other quantities. The variations of partial derivatives stand for

$$\begin{aligned}&\Delta\left(\frac{\partial S}{\partial U_\alpha}\right)^0_{V,N} = \\ &\quad \left(\frac{\partial^2 S}{\partial U^2}\right)^0_{V,N}\Delta U_\alpha + \left[\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial U}\right)_{V,N}\right]^0_{U,N}\Delta V_\alpha \\ &\quad + \sum_j \left[\frac{\partial}{\partial N_j}\left(\frac{\partial S}{\partial U}\right)_{V,N}\right]^0_{U,V}\Delta N_{j\alpha}\end{aligned}$$

and similarly for other partial derivatives.

In an equilibrium

$$\left(\frac{\partial S}{\partial U}\right)^0 = \left(\frac{\partial S}{\partial V}\right)^0 = \left(\frac{\partial S}{\partial N_j}\right)^0 = 0,$$

so

$$\begin{aligned}&\Delta S_\alpha = \\ &\quad \frac{1}{2}\Bigg\{\Delta\left(\frac{\partial S}{\partial U_\alpha}\right)^0_{V,N}\Delta U_\alpha + \Delta\left(\frac{\partial S}{\partial V_\alpha}\right)^0_{U,N}\Delta V_\alpha \\ &\qquad + \sum_j \Delta\left(\frac{\partial S}{\partial N_{j\alpha}}\right)^0_{U,V}\Delta N_{j\alpha}\Bigg\}.\end{aligned}$$

This can be rewritten as

$$\begin{aligned}&\Delta S_\alpha = \\ &\quad \frac{1}{2}\Bigg\{\Delta\left(\frac{1}{T_\alpha}\right)\Delta U_\alpha + \Delta\left(\frac{p_\alpha}{T_\alpha}\right)\Delta V_\alpha \\ &\qquad - \sum_j \Delta\left(\frac{\mu_{j\alpha}}{T_\alpha}\right)\Delta N_{j\alpha}\Bigg\}.\end{aligned}$$

Using the first law we get

$$\begin{aligned}\Delta S = \frac{1}{2T}\sum_\alpha\Bigg\{ & -\Delta T_\alpha \Delta S_\alpha + \Delta p_\alpha \Delta V_\alpha \\ & - \sum_j \Delta\mu_{j\alpha}\Delta N_{j\alpha}\Bigg\}.\end{aligned}$$

This can be further written as

$$\begin{aligned}\Delta S = -\frac{1}{2T}\sum_\alpha\Bigg\{ & \frac{C_V}{T}(\Delta T_\alpha)^2 + \frac{1}{\kappa_T V}[(\Delta V_\alpha)^2_{N_\alpha}] \\ & + \left(\frac{\partial \mu}{\partial N}\right)^0_{p,T}(\Delta N_\alpha)^2\Bigg\},\end{aligned}$$

where

$$(\Delta V_\alpha)_{N_\alpha} = \left(\frac{\partial V}{\partial T}\right)^0_{N,p}\Delta T_\alpha + \left(\frac{\partial V}{\partial p}\right)^0_{N,T}\Delta p_\alpha.$$

Since $\Delta S \le 0$, we must have

$$C_V \ge 0,\ \kappa_T \ge 0,\ \frac{\partial \mu}{\partial N} \ge 0.$$

Application of thermodynamics

Classical ideal gas

From the equation of state

$$pV = Nk_BT$$

we obtain the mechanical response functions

$$\begin{aligned}\alpha_p &= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N} = \frac{Nk_B}{Vp} = \frac{1}{T}\\ \kappa_T &= -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} = \frac{Nk_BT}{Vp^2} = \frac{1}{p}.\end{aligned}$$

Thermal response functions cannot be derived from the equation of state. Empirically we have

$$C_V = \frac{1}{2}fk_BN.$$

Here $\frac{1}{2}fk_B$ is the specific heat capacity/molecule and f is the number of degrees of freedom of the molecule.

Atoms/molecule	f	translations	rotations
1	3	3	0
2	5	3	2
poly	6	3	3

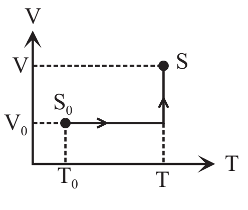
For real gases $f = f(T, p)$.

Entropy

$$\begin{aligned}dS &= \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV\\ &= \frac{1}{T}C_V dT + \left(\frac{\partial p}{\partial T}\right)_V dV,\end{aligned}$$

since according to Maxwell relations

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V.$$



Integrating we get

$$\begin{aligned}S &= S_0 + \int_{T_0}^{T} dT\,\frac{C_V}{T} + \int_{V_0}^{V} dV\,\frac{Nk_B}{V}\\ &= S_0 + C_V\ln\frac{T}{T_0} + Nk_B\ln\frac{V}{V_0}\end{aligned}$$

or

$$S = S_0 + Nk_B\ln\left[\left(\frac{T}{T_0}\right)^{f/2}\frac{V}{V_0}\right].$$

Note A contradiction with the third law: $S \to -\infty$, when $T \to 0$.

Internal energy

We substitute into the firs law

$$dU = T\,dS - p\,dV$$

the differential

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV,$$

and get

$$dU = C_V dT + \left[T\left(\frac{\partial S}{\partial V}\right)_T - p\right] dV.$$

According to a Maxwell relations and to the equation of state we have

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \frac{Nk_B}{V} = \frac{p}{T},$$

so

$$dU = C_V dT$$

and

$$U = U_0 + C_V(T - T_0) = U_0 + \frac{1}{2}fk_BN(T - T_0).$$

If we choose $U_0 = C_VT_0$, we get for the internal energy

$$U = \frac{1}{2}fk_BNT.$$

Now

$$C_p = C_V + VT\,\frac{\alpha_p^2}{\kappa_T}$$

or

$$C_p = Nk_B\left(\frac{1}{2}f + 1\right)$$

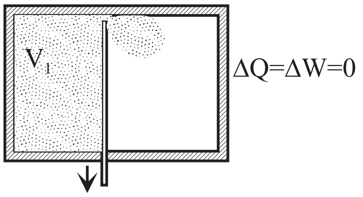
or

$$C_p = \gamma C_V,$$

where γ is the *adiabatic constant*

$$\gamma = C_p/C_V = (f + 2)/f.$$

Free expansion of gas



In the process $V_1 \to V_2$ and $\Delta Q = \Delta W = 0$, so $\Delta U = 0$. Process is irreversible.

a) Ideal gas

Now

$$U = \frac{1}{2}fk_BTN,$$

so $T_1 = T_2$, because $U_1 = U_2$. The cange in the entropy is thus

$$\Delta S = N k_B \ln \frac{V_2}{V_1}.$$

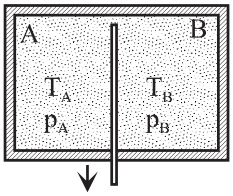
b) Other material
The internal energy (and the number of particle) being constant ($\mathrm{d}U = 0$) we obtain from the expression

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V$$

for the *Joule coefficient* $\left(\frac{\partial T}{\partial V}\right)_{U,N}$ the form

$$\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_{U,N} &= -\frac{\left(\frac{\partial U}{\partial V}\right)_T}{\left(\frac{\partial U}{\partial T}\right)_V} \\ &= \frac{1}{C_V}\left(p - T\,\frac{\alpha_p}{\kappa_T}\right). \end{aligned}$$

Mixing entropy



Suppose that initially $p_A = p_B = p$ and $T_A = T_B = T$.
The process is adiabatic so $\Delta Q = 0$.
In a mixture of ideal gases every component satisfies the state equation

$$p_j V = N_j k_B T.$$

The concentration of the component j is

$$x_j = \frac{N_j}{N} = \frac{p_j}{p},$$

where the total pressure p is

$$p = \sum_j p_j.$$

Way 1
Each constituent gas expands in turn into the volume V. Since $p_A = p_B$ and $T_A = T_B$, we have $V_j = V x_j$. The change in the entropy is (see the free expansion of a gas)

$$\Delta S = \sum_j N_j k_B \ln \frac{V}{V_j}$$

or

$$\Delta S_{\text{mix}} = -N k_B \sum_j x_j \ln x_j.$$

Now $\Delta S_{\text{mix}} \geq 0$, since $0 \leq x_j \leq 1$.
Way 2
For a process taking place in constant pressure and temperature the Gibbs function is the suitable potential:

$$\begin{aligned} G &= U - TS + pV \\ &= \frac{1}{2} f k_B T N - TS + pV = \cdots \\ &= N k_B T[\phi(T) + \ln p] = N\mu(p, T), \end{aligned}$$

where

$$\phi(T) = \frac{\mu^0}{k_B T} - \xi - (\frac{f}{2} + 1)\ln T.$$

Before mixing

$$G_{(\mathrm{b})} = \sum_j N_j k_B T[\phi_j(T) + \ln p]$$

and after mixing

$$G_{(\mathrm{a})} = \sum_j N_j k_B T[\phi_j(T) + \ln p_j],$$

so the change in the Gibbs function is

$$\begin{aligned} \Delta G_{(\mathrm{mix})} &= G_{(\mathrm{a})} - G_{(\mathrm{b})} = \sum_j N_j k_B T \ln \frac{p_j}{p} \\ &= \sum_j N_j k_B T \ln x_j. \end{aligned}$$

Because

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,\{N_j\}},$$

we get for the mixing entropy

$$\Delta S_{\text{mix}} = S_{(\mathrm{a})} - S_{(\mathrm{b})} = -\sum_j N_j k_B \ln x_j.$$

Gibbs' paradox: If $A \equiv B$, i.e. the gases are identical no changes take place in the process. However, according to the former discussion, $\Delta S > 0$. The contradiction can be removed by employing quantum statitics of identical particles.

Chemical reaction

Consider for example the chemical reaction

$$2\,\mathrm{H_2S} + 3\,\mathrm{O_2} \rightleftarrows 2\,\mathrm{H_2O} + 2\,\mathrm{SO_2}.$$

In generall the *chemical reaction formula* is written as

$$0 = \sum_j \nu_j M_j.$$

Here $\nu_j \in \mathcal{I}$ are the *stoichiometric coefficients* and M_j stand for the molecular species.

Example

j	A	B	C	D
M_j	$\mathrm{H_2S}$	$\mathrm{O_2}$	$\mathrm{H_2O}$	$\mathrm{SO_2}$
ν_j	-2	-3	2	2

We define the *degree of reaction* ξ so that

$$\mathrm{d}N_j = \nu_j \mathrm{d}\xi.$$

When ξ increments by one, one reaction of the reaction formula from left to right takes place.
Convention: When $\xi = 0$ the reaction is as far left as it can be. Then we always have

$$\xi \geq 0.$$

We suppose that p and T are constant in the reaction. Then a suitable potential is the Gibbs function

$$G = U - TS + pV = \sum_j \mu_j N_j.$$

Its differential is

$$\mathrm{d}G = \sum_j \mu_j \mathrm{d}N_j = \mathrm{d}\xi \sum_j \nu_j \mu_j.$$

We define

$$\Delta_{\mathrm{r}} G \equiv \Delta_{\mathrm{r}} \equiv \left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \sum_j \nu_j \mu_j.$$

Δ_{r} is thus the change in the Gibbs function per one reaction.
Since (p, T) is constant G has a minimum at an equilibrium. The equilibrium condition is thus

$$\Delta_{\mathrm{r}} G^{\mathrm{eq}} = \sum_j \nu_j \mu_j^{\mathrm{eq}} = 0.$$

In a nonequilibrium $\mathrm{d}G/\mathrm{d}t < 0$, so if $\Delta_{\mathrm{r}} > 0$ we must have $\mathrm{d}\xi/\mathrm{d}t < 0$, i.e. the reaction proceeds to left and vice versa.
We assume that the components obey the ideal gas equation of state. Then

$$\mu_j = k_B T[\phi_j(T) + \ln p + \ln x_j],$$

where

$$\phi_j(T) = \frac{\mu_j^0}{k_B T} - \eta_j - (1 + \frac{1}{2} f_j) \ln T.$$

So

$$\Delta_{\mathrm{r}} G = k_B T \sum_j \nu_j \phi_j(T) + k_B T \ln\left(p^{\sum \nu_j} \prod x_j^{\nu_j}\right).$$

The equilibrium condition can now be written as

$$\prod_j x_j^{\nu_j} = p^{-\sum_j \nu_j} K(T),$$

where

$$K(T) = e^{-\sum_j \nu_j \phi_j(T)}$$

is the *equilibrium constant* of the reaction. The equilibrium condition is called the *law of mass action.*
The *reaction heat* is the change of heat $\Delta_{\mathrm{r}} Q$ per one reaction to right. A reaction is

- *Endothermic*, if $\Delta_{\mathrm{r}} Q > 0$ i.e. the reaction takes heat.
- *Exothermic*, if $\Delta_{\mathrm{r}} Q < 0$ i.e. the reaction releases heat.

We write $\Delta_{\mathrm{r}} G$ as

$$\Delta_{\mathrm{r}} G = -k_B T \ln K(T) + k_B T \sum_j \nu_j \ln p x_j.$$

Now

$$\begin{aligned} \Delta Q &= \Delta U + \Delta W = \Delta U + p\,\Delta V = \Delta(U + pV) \\ &= \Delta H, \end{aligned}$$

since $\Delta p = 0$.
When the total amount matter is constant

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p$$

holds in a reversible process and

$$\begin{aligned} \mathrm{d}\left(\frac{G}{T}\right) &= \frac{1}{T}\,\mathrm{d}G - \frac{G}{T^2}\,\mathrm{d}T = -\left(\frac{G}{T^2} + \frac{S}{T}\right)\mathrm{d}T + \frac{V}{T}\,\mathrm{d}p \\ &= -\frac{H}{T^2}\,\mathrm{d}T + \frac{V}{T}\,\mathrm{d}p, \end{aligned}$$

because $G = H - TS$. We see that

$$H = -T^2 \left[\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right]_{p,N}.$$

Now

$$\frac{\partial}{\partial T}\left(\frac{\Delta_{\mathrm{r}} G}{T}\right) = -k_B \frac{\mathrm{d}}{\mathrm{d}T} \ln K(T),$$

so that

$$\Delta_{\mathrm{r}} H = k_B T^2 \frac{\mathrm{d}}{\mathrm{d}T} \ln K(T).$$

This expression is known as the *reaction heat.*

Phase equilibrium

In a system consisting of several phases the equilibrium conditions for each pair (A and B) of phases are

$$\begin{aligned} T_A &= T_B = T \\ p_A &= p_B = p \\ \mu_{jA} &= \mu_{jB},\ j = 1, \ldots, H, \quad (*) \end{aligned}$$

where H is the number of particle species in the system.
Let us assume that the number of phases is F, so for each species there are $F - 1$ independent conditions $(*)$. Now $\mu_{i\alpha} = \mu_{i\alpha}(p, T, \{N_{j\alpha}\})$. Because the chemical potential is an intensive quantity it depends only on relative fractions, so

$$\mu_{j\alpha} = \mu_{j\alpha}(p, T, x_{1\alpha}, \ldots, x_{H-1,\alpha}),$$

and the conditions $(*)$ take the form

$$\begin{aligned} &\mu_{1A}(p, T, x_{1A}, \ldots, x_{H-1,A}) = \\ &\qquad \mu_{1B}(p, T, x_{1B}, \ldots, x_{H-1,B}) \\ &\vdots \\ &\mu_{HA}(p, T, x_{1A}, \ldots, x_{H-1,A}) = \\ &\qquad \mu_{HB}(p, T, x_{1B}, \ldots, x_{H-1,B}). \end{aligned}$$

There are

- $M = (H-1)F + 2$ variables,
- $Y = H(F-1)$ equations.

The simultaneous equations can have a solution only if $M \geq Y$ or

$$F \leq H + 2.$$

This condition is known as the *Gibbs phase rule*.
For *pure matter* the equilibrium condition

$$\mu_A(p,T) = \mu_B(p,T)$$

defines in the (p,T)-plane a *coexistence curve*. If the phase B is in equilibrium with the phase C we get another curve

$$\mu_B(p,T) = \mu_C(p,T).$$

The phases A, B can C can be simultaneously in equilibrium in a crossing point, so called *triple point*, of these curves.

Phase transitions

In a phase transition the chemical potential

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{p,T}$$

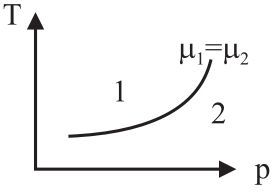
is continuous. Instead

$$S = -\left(\frac{\partial G}{\partial T}\right)_{p}$$

and

$$V = \left(\frac{\partial G}{\partial p}\right)_{T}$$

are not necessarily continuous.
A transition is of *first order*, if the first order derivatives (S, V) of G are discontinuous and of *second order*, if the second order derivatives are discontinuous. Otherwise the transition is *continuous*



In a first order transition from a phase 1 to a phase 2

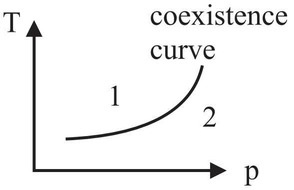
$$\begin{aligned}\Delta S &= -\left(\frac{\partial G}{\partial T}\right)_{p}^{(2)} + \left(\frac{\partial G}{\partial T}\right)_{p}^{(1)}\\ \Delta V &= \left(\frac{\partial G}{\partial p}\right)_{T}^{(2)} - \left(\frac{\partial G}{\partial p}\right)_{T}^{(1)}.\end{aligned}$$

When we cross a coexistence curve p and T stay constant, so

$$\begin{aligned}\Delta Q &= T\,\Delta S = \Delta U + p\,\Delta V = \Delta(U + pV)\\ &= \Delta H.\end{aligned}$$

ΔQ is called the *phase transition heat* or the *latent heat*.
Note First order transitions are associated with the heat of phase transitions but not the higher order transitions.

Coexistence



On the coexistence curve

$$G_1(p,T,N) = G_2(p,T,N)$$

and

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p$$

when the number of particles N is constant. Along the curve

$$G_1(p+\mathrm{d}p, T+\mathrm{d}T, N) = G_2(p+\mathrm{d}p, T+\mathrm{d}T, N),$$

so that

$$-S_1\mathrm{d}T + V_1\mathrm{d}p = -S_2\mathrm{d}T + V_2\mathrm{d}p$$

or on the curve

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{\Delta S}{\Delta V} = \frac{T^{-1}\Delta H}{\Delta V}$$

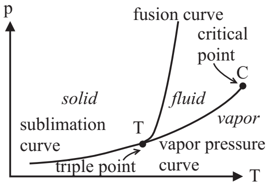
and we end up with the *Clausius-Clapeyron equation*

$$\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_{\mathrm{coex}} = \frac{1}{T}\,\frac{\Delta H}{\Delta V}.$$

Here $\Delta H = H_2 - H_1$ and $\Delta V = V_2 - V_1$.

Examples

a) Vapor pressure curve



We consider the transition

$$\text{liquid} \rightarrow \text{vapor}.$$

Supposing that we are dealing with ideal gas we have

$$\Delta V = V_{\mathrm{v}} = \frac{Nk_BT}{p},$$

since

$$V_{\mathrm{l(iquid)}} \ll V_{\mathrm{v(apor)}}.$$

Because the vaporization heat (the phase transition heat) ΔH_{lv} is roughly constant on the vapor pressure curve we have

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H_{\mathrm{lv}} p}{N k_B T^2}.$$

Integration gives us

$$p = p_0 e^{-\Delta H_{\mathrm{lv}}/N k_B T}.$$

b) Fusion curve
Now

$$\Delta V_{\mathrm{ls}} = V_{\mathrm{l(iquid)}} - V_{\mathrm{s(olid)}}$$

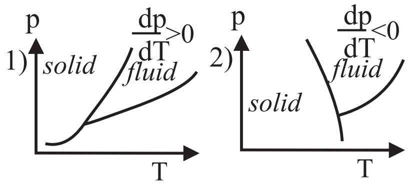
can be positive or negative (for example H_2O).
According to the Clausius-Clapeyron equation

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H_{\mathrm{ls}}}{T\,\Delta V_{\mathrm{ls}}}$$

we have

$$\frac{\mathrm{d}p}{\mathrm{d}T} > 0, \quad \text{if } \Delta V_{\mathrm{ls}} > 0 \qquad 1)$$

$$\frac{\mathrm{d}p}{\mathrm{d}T} < 0, \quad \text{if } \Delta V_{\mathrm{ls}} < 0 \qquad 2) \quad .$$



We see that when the pressure is increased in constant temperature the system

1) drifts "deeper" into the solid phase,

2) can go from the solid phase to the liquid phase.

c) Sublimation curve
Now

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p = C_p \mathrm{d}T + V(1 - T\alpha_p)\,\mathrm{d}p,$$

since $S = S(p, T)$ and using Maxwell relations and definitions of thermodynamic response functions

$$\mathrm{d}S = \left(\frac{\partial S}{\partial p}\right)_T \mathrm{d}p + \left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T = -\left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p + \frac{C_p}{T}\,\mathrm{d}T.$$

The vapor pressure is small so $\mathrm{d}p \approx 0$, and

$$\begin{aligned} H_{\mathrm{s}} &= H_{\mathrm{s}}^0 + \int_0^T C_p^{\mathrm{s}} \mathrm{d}T & \qquad \text{solid phase} \\ H_{\mathrm{v}} &= H_{\mathrm{v}}^0 + \int_0^T C_p^{\mathrm{v}} \mathrm{d}T & \qquad \text{vapor (gas).} \end{aligned}$$

Let us suppose that the vapor satisfies the ideal gas state equation. Then

$$\Delta V_{\mathrm{vs}} = \frac{N k_B T}{p} - V_{\mathrm{s}} \approx \frac{N k_B T}{p},$$

so

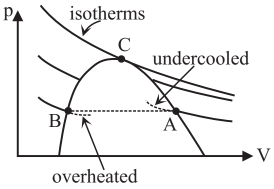
$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H_{\mathrm{vs}}}{T\,\Delta V_{\mathrm{vs}}} \approx \frac{p\,\Delta H_{\mathrm{vs}}}{N k_B T^2},$$

where $\Delta H_{\mathrm{vs}} = H_{\mathrm{s}} - H_{\mathrm{v}}$.
For a mono atomic ideal gas $C_p = \frac{5}{2} k_B N$, so that

$$\ln p = -\frac{\Delta H_{\mathrm{vs}}^0}{N k_B T} + \frac{5}{2}\ln T - \frac{1}{k_B N} \int \frac{\int_0^T C_p^{\mathrm{s}} \mathrm{d}T'}{T^2}\,\mathrm{d}T + \text{constant}.$$

Here ΔH_{vs}^0 is the sublimation heat at 0 temperature and pressure.

Coexistence range



Matter is mechanically stable only if $\frac{\mathrm{d}V}{\mathrm{d}p} < 0$. Thus the range of stability lies outside of the points A and B. Overheated liquid and undercooled vapor are metastable. According to the Gibbs-Duhem relation

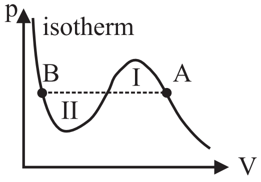
$$\mathrm{d}\mu = -\frac{S}{N}\,\mathrm{d}T + \frac{V}{N}\,\mathrm{d}p$$

we have on an isotherm

$$\mathrm{d}\mu = \frac{V}{N}\,\mathrm{d}p.$$

Thus, when the phases A and B are in equilibrium,

$$\mu_A - \mu_B = \int_A^B \frac{V}{N}\,\mathrm{d}p = 0.$$



Maxwell's construction: The points A and B have to be chosen so that the area I = area II.