

Introduction

- Thermodynamics: phenomenological description of equilibrium bulk properties of matter in terms of only a few “state variables” and thermodynamical laws.
- *Statistical physics*: microscopic foundation of thermodynamics
- $\sim 10^{23}$ degrees of freedom \rightarrow 2–3 state variables!
- “Everything should be made as simple as possible, but no simpler” (A. Einstein)

Summary of contents:

- Review of thermodynamics
- Thermodynamical potentials
- Phase space and probability
- Quantum mechanical ensembles
- Equilibrium ensembles
- Ideal fluids
- Bosonic systems
- Fermionic systems
- Interacting systems
- Phase transitions and critical phenomena

1. Foundations of thermodynamics

1.1. Fundamental thermodynamical concepts

System : macroscopic entity under consideration.

Environment : world outside of the system (infinite).

Open system : can exchange matter and heat with the environment.

Closed system : can exchange heat with the environment while keeping the number of particles fixed.

Isolated system : can exchange neither matter nor heat with the environment. Can (possibly) still do work by e.g. expanding.

Thermodynamical equilibrium:

- No macroscopic changes.
- Uniquely described by (a few) external variables of state.
- System forgets its past: no memory effects, no hysteresis.
- Often the term *global equilibrium* is used, as opposed to local equilibrium, which is not full equilibrium at all (next page)!

Nonequilibrium:

- Generally much more complicated than equilibrium state.
- Simplest case: isolated systems each in an equilibrium state.
- In a *local thermodynamical equilibrium* small regions are locally in equilibrium, but neighbour regions in different equilibria \Rightarrow particles, heat etc. will flow. Example: fluid (water) with non-homogeneous temperature.
- Stronger nonequilibrium systems usually *relax* to a local equilibrium.

Degrees of freedom (d.o.f.) is the number of quantities needed for the exact description of the microscopic state.

Example: classical ideal gas with N particles: $3N$ coordinates (x, y, z) , $3N$ momenta (p_x, p_y, p_z) .

State variables are parameters characterizing the macroscopic thermodynamical state. These are all *extensive* or *intensive*:

Extensive variable: change value when the size (spatial volume and the number of degrees of freedom) is changed: volume V , particle number N , internal energy U , entropy S , total magnetic moment $\int d^3r \mathbf{M}$.

Intensive variable: independent of the size of the system, and can be determined for every semimicroscopical volume element: e.g. temperature T , pressure p , chemical potential μ , magnetic field \mathbf{H} , ratios of extensive variables like $\rho = N/V$, $s = S/N$, ...

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

Example: pressure p and volume V ; change in internal energy U when V is changed (adiabatically, at constant S) is $dU = -pdV$.

Process is a change in the state.

Reversible process: advances via states infinitesimally close to equilibrium, *quasistatically* ("slow process"). The direction of a reversible process can be reversed, obtaining the initial state (for system + environment!)

Isothermal process : T constant.

Isobaric process : p constant.

Isochoric process : V constant.

Isentropic or adiabatic process: S constant.

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

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

1.2. State variables and exact differentials

Let us suppose that, for example, the state of the system can be uniquely described by state variables T , V ja N . Other state variables are then their unique functions:

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

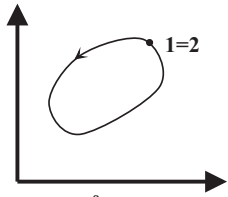
By applying differential calculus, the differential of p , for example, is

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

⋮

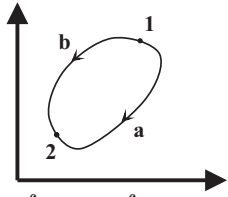
The differentials of state variables, dp , dT , dV , ..., are **exact differentials**. These have the following properties

(A) Their total change evaluated over a closed path vanishes:



$$\oint_{1 \rightarrow 2} dp = \oint_{1 \rightarrow 2} dU = \dots = 0.$$

(B) The total change of an exact differential is independent on the path of integration:



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

so that we can write

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

Exact differentials

Let us denote by dF a differential which is not necessarily exact (i.e. integrals can depend on the path). Assuming it depends on 2 variables x , y , the differential

$$dF = F_1(x, y) dx + F_2(x, y) dy$$

is **exact differential** 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

$$\int_1^2 dF = F(2) - F(1)$$

is independent on the path, and integrable. In this case (x, F_1) and (y, F_2) are pairs of conjugated variables with respect to F .

Examples: are the following differentials exact?

$$dF = y dx + x dy$$

$$dF = x dx + x dy$$

All physical state variables are exact differentials! This will enable us to derive various identities between state variables.

Integrating factor

If $dF = F_1 dx + F_2 dy$ is not exact, there exists an *integrating factor* $\lambda(x, y)$ so that in the neighbourhood of the point (x, y)

$$\lambda dF = \lambda F_1 dx + \lambda F_2 dy = df$$

is an exact differential. λ and f are state variables.
 Example: find λ for the differential

$$dF = x dx + x dy.$$

Legendre transformations

Legendre transformations can be used to make changes in the set of the independent 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

$$g = f - y f_y = f - y z.$$

(Note: z, y is a conjugated pair with respect to f !) 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 $f \rightarrow g$ there is the inverse transformation $g \rightarrow f$

$$f = g - z g_z = g + y z.$$

Often needed identities

Let $F = F(x, y)$, $x = x(y, z)$, $y = y(x, z)$ and $z = z(x, y)$. If we want to give F in terms of (x, z) , we can write

$$F(x, y) = F(x, y(x, z)).$$

Applying differential rules we obtain identities

$$\begin{aligned} \left(\frac{\partial F}{\partial x}\right)_z &= \left(\frac{\partial F}{\partial x}\right)_y + \left(\frac{\partial F}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \\ \left(\frac{\partial F}{\partial z}\right)_x &= \left(\frac{\partial F}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x \end{aligned}$$

One can show that

$$\begin{aligned} \left(\frac{\partial x}{\partial y}\right)_z &= \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} \\ \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y &= -1 \end{aligned}$$

and

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{\left(\frac{\partial F}{\partial y}\right)_z}{\left(\frac{\partial F}{\partial x}\right)_z}.$$

1.3. Equations of state

Encodes (some of the) physical properties of the equilibrium system. Usually these relate “mechanical” readily observable variables, like p, T, N, V ; not “internal” variables like S , internal energy U etc. A typical example: pressure of some gas as a function of T and density ρ .

Some examples:

Classical ideal gas

$$pV = Nk_B T$$

where N = number of molecules

T = absolute temperature

$k_B = 1.3807 \cdot 10^{-23} \text{J/K}$ = Boltzmann constant. 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

$$pV = Nk_B T,$$

where now

$$N = \sum_{i=1}^m N_i$$

and

$$p = \sum_i p_i, \quad p_i = N_i k_B T / V,$$

where p_i is the partial pressure of the i :th component

Virial expansion of real gases

When the interactions between gas molecules are taken into account, the ideal gas law receives corrections which are suppressed by powers of density $\rho = N/V$:

$$p = k_B T [\rho + \rho^2 B_2(T) + \rho^3 B_3(T) + \dots]$$

Here 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 (potential $\sim (r/r_0)^6$) 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

$$p'V' = Nk_B T$$

so that

$$\begin{aligned} V' &= V - Nb \\ p &= p' - a\rho^2 = \text{true pressure.} \end{aligned}$$

then

$$(p + a\rho^2)(V - Nb) = Nk_B T.$$

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/m²]

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

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

Surface tension

$$\sigma = \sigma_0 \left(1 - \frac{t}{t'} \right)^n$$

t = temperature °C

t' and n = experimental constants,

$$1 \lesssim n \lesssim 2$$

σ_0 = surface tension when $t = 0^\circ\text{C}$.

Electric polarization

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

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

where

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

In homogenous dielectric material one has

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

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 \mathbf{H} we write

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

where

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

Polarization obeys roughly *Curie's law*

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

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 .

Laws of thermodynamics

Thermodynamics is based upon 4 laws (these can be derived from statistical physics, but in thermodynamics these are considered “fundamental”).

1.4. 0th law of thermodynamics

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.

1.5. Work

Before we discuss the 1st law, let us introduce the concept of *Work*. Work is exchange of such “noble” energy (as opposed to exchange of heat or matter) 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 environment*. **Example:** pVT system

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

Note: dW is *not* an exact differential: the work done by the system is not a function of the final state of the system (need to know the history!). Instead

$$\frac{1}{p}dW = dV$$

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

Example:

$$dW = p dV - \sigma A dL - \mathbf{E} \cdot d\mathbf{P} - \mathbf{H} \cdot d\mathbf{M}.$$

In general

$$dW = \sum_i f_i dX_i = \mathbf{f} \cdot d\mathbf{X},$$

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

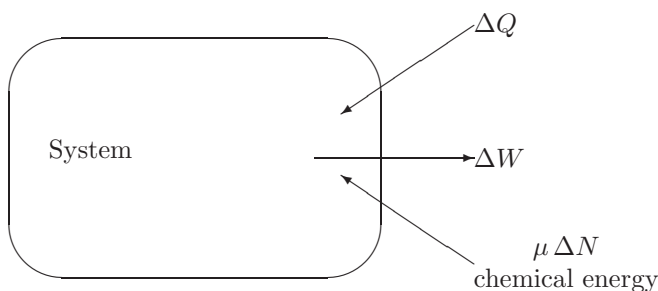
1.6. 1st law of thermodynamics

Total energy is conserved

In addition to work a system can exchange *heat* (*thermal energy*) or *chemical energy*, associated with the exchange of matter, with its environment. Thermal energy is related to the energy of the thermal stochastic motion of microscopic particles.

The total energy of a system is called **internal energy** U .

Sign conventions:



If the system can exchange heat and particles and do work, the energy conservation law gives the change of the internal energy

$$dU = dQ - dW + \mu dN,$$

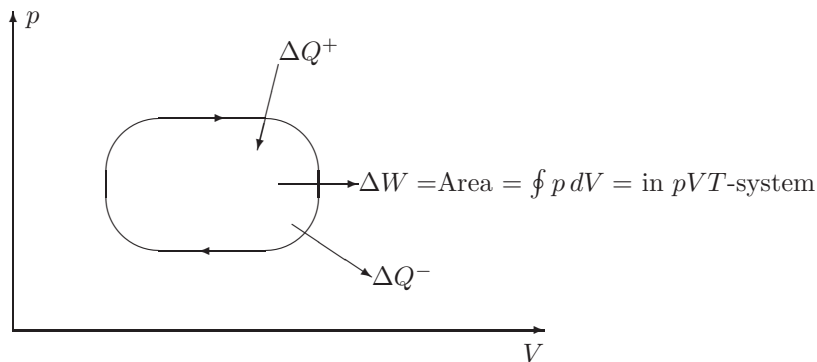
where μ is the chemical potential. More generally,

$$dU = dQ - \mathbf{f} \cdot d\mathbf{X} + \sum_i \mu_i dN_i.$$

U is a state variable, i.e. dU is exact.

Cyclic process

In a cyclic process the system returns to the original state. Now $\oint dU = 0$, so $\Delta W = \Delta Q$ (no change in thermal energy). Now ΔQ^+ is the heat absorbed by the system during one cycle and $-\Delta Q^- (> 0)$ is the heat released.



The total change of heat is

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

The *efficiency* of a heat engine ($\Delta W > 0$) is work/(heat taken):

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

1.7. 2nd law of thermodynamics

2nd law can be stated in various (historical) ways:

- Heat flows spontaneously from high temperatures to low temperatures.
- Heat cannot be transferred from a cooler heat reservoir to a warmer one without other changes.
- In a cyclic process it is not possible to convert all heat taken from the hotter heat reservoir into work.
- It is not possible to reverse the evolution of a system towards thermodynamical equilibrium without converting work to heat.
- The change of the total entropy of the system and its environment is positive and can be zero only in reversible processes.

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

We define the *efficiency* as

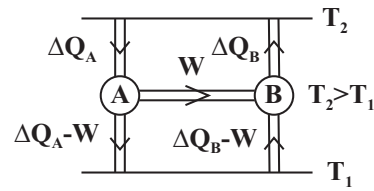
$$\eta = \frac{\Delta W}{\Delta Q_2} = 1 - \frac{\Delta Q_1}{\Delta Q_2}.$$

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 efficiencies 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 b). So we must have

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

By running the engines backwards 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*.

Similarly, it follows that the *Carnot engine has the highest efficiency among all engines* (also irreversible) working between given temperatures: assume that engine \mathcal{A} in previous figure is some other engine than Carnot. Then the argument above implies that $\eta_{\mathcal{A}} \leq \eta_{\mathcal{B}}$. If \mathcal{A} is *not* reversible, efficiency is not necessarily the same while running the system backwards and the inequality remains in force; if it is reversible, reversing the process gives $\eta_{\mathcal{A}} = \eta_{\mathcal{B}}$.

Note: The efficiency does not depend on the realization of the cycle (e.g. the working substance). Only reversibility is essential! \Rightarrow The efficiency depends only on the temperatures of the heat reservoirs.

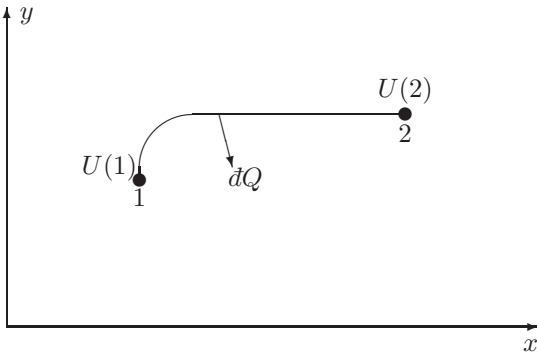
Defining temperature scale via Carnot engines: Let us consider Carnot's cycle between temperatures T_3 and T_1 . Now

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

where we have the identity

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

We consider the infinitesimal process



Now

$$dQ = dU + dW = dU + \mathbf{f} \cdot d\mathbf{X},$$

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

$$\frac{1}{T} dQ = dS$$

is exact. The state variable S is *entropy* and T turns out to be *temperature* (on an absolute scale) The second law (e) can now be written as

$$\boxed{\frac{dS_{\text{tot}}}{dt} \geq 0},$$

where S_{tot} is the entropy of the system + environment. For the entropy of the system only we have

$$dS \geq \frac{1}{T} dQ,$$

where the equality holds only for reversible processes. The entropy of the system can decrease, but the total entropy always increases (or stays constant).

For reversible processes the first law can be rewritten as

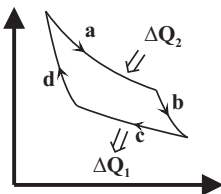
$$\boxed{dU = dQ - dW + \mu dN = T dS - p dV + \mu dN.}$$

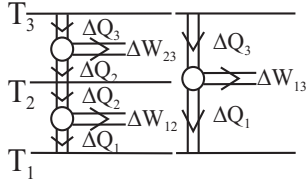
1.8. Carnot cycle

Illustrates the concept of entropy. The Carnot engine \mathcal{C} consists of reversible processes

- a) isothermal T_2 $\Delta Q_2 > 0$
- b) adiabatic $T_2 \rightarrow T_1$ $\Delta Q = 0$
- c) isothermal T_1 $\Delta Q_1 > 0$
- d) adiabatic $T_1 \rightarrow T_2$ $\Delta Q = 0$

Now $\Delta U = 0$, so $\Delta W = \Delta Q_2 - \Delta Q_1$ (wrong sign here, for simplicity).





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

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

This (theoretical) definition was first used by Kelvin, and it gives us our familiar absolute temperature scale, up to a scale factor.

(This is by no means unique; one could also use $f(t_2, t_1) = [t_2/t_1]^a$, with any $a \neq 0$, this would just give us a different temperature scale $t = \text{const.} \times T^{1/a}$.)

The Carnot cycle satisfies

$$\oint \frac{dQ}{T} = 0,$$

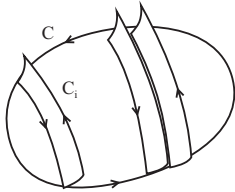
since, during the isothermal part a ,

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

and part c

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

This is valid also for an arbitrary reversible cycle



because

$$\oint_C \frac{dQ}{T} = \sum_i \oint_{C_i} \frac{dQ}{T} = 0.$$

So

$$dS = \frac{dQ}{T}$$

is exact and the *entropy* S and the temperature T are state variables. 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

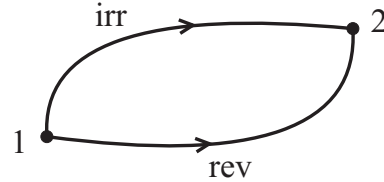
$$\frac{\Delta Q_2}{T_2} - \frac{\Delta Q_1}{T_1} < 0.$$

Thus for an arbitrary cycle we have

$$\oint \frac{dQ}{T} \leq 0, \quad (*)$$

where the equality holds only for reversible processes. Because entropy S is a state variable, it cannot depend on the integration path. Thus, for an arbitrary process $1 \rightarrow 2$ the change of the entropy can be obtained from the formula

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



According to the formula (*) we have

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

or

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

This is usually written as

$$dS \geq \frac{dQ}{T},$$

and the equality is valid only for reversible processes. For an isolated system ($\Delta Q = 0$, e.g. system + environment!) we have

$$\Delta S \geq 0.$$

Thus, for an irreversible process,

$$\begin{aligned} \Delta Q_{\text{irr}} &\leq \Delta Q_{\text{rev}} = T\Delta S, \\ \Delta W_{\text{irr}} = \Delta Q_{\text{irr}} - \Delta U &\leq \Delta W_{\text{rev}} = \mathbf{f} \cdot d\mathbf{X} \end{aligned}$$

where “rev” is a hypothetical reversible process connecting the initial and final states of “irr”-trajectory. Note the sign conventions: ΔW work done by the system; ΔQ heat absorbed by the system. $\Delta W_{\text{irr}} \leq \Delta W_{\text{rev}}$ means less work done by “irr” ($\Delta W > 0$) or more work done to it ($\Delta W < 0$).

1.9. 3rd law of thermodynamics

Nernst's law (1906):

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

A less strong form can be stated as:

When the maximum temperature occurring in the process from a state a to a state b approaches zero, also the entropy change $\Delta S_{a \rightarrow b} \rightarrow 0$.

Note: There are systems whose entropy at low temperatures is larger than true equilibria would allow. This is due to very slow relaxation time

2. Thermodynamic potentials

2.1. Fundamental equation

According to the first law (in a TVN -system, generalizes easily), for reversible processes

$$\boxed{dU = T dS - p dV + \mu dN}. \quad (*)$$

S , V and N can be considered to be *natural variables* of the internal energy U , i.e. $U = U(S, V, N)$. Furthermore, from the law (*) one can read the relations

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

Scaling law of extensive variables: all extensive variables must be linear functions of system size V (and each other). Now U , S , V and N are extensive so we have

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N) \quad \forall \lambda. \quad (***)$$

Taking a derivative of (***) wrt. λ , we obtain 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 in (**) this takes the form

$$\boxed{U = TS - pV + \mu N}$$

or

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

This is called the *fundamental equation*.

2.2. 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

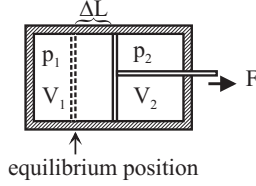
$$T \Delta S > \Delta Q = \Delta U + \Delta W,$$

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 ($\Delta Q = 0$)



We partition ΔW into the components

$$\int p dV = \left[\begin{array}{l} \text{work due to the} \\ \text{change of the total} \\ \text{volume } (= 0) \end{array} \right]$$

$$\Delta W_{\text{free}} = \left[\begin{array}{l} \text{work done by the} \\ \text{gas against the} \\ \text{force } \mathbf{F} \end{array} \right].$$

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

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

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 exchangeable 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

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

If the system does no work, $\Delta U \leq 0$, i.e. the system tends to minimize its internal energy.

2.3. Enthalpy

Using the Legendre transform

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

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

$$\boxed{H = U + pV}$$

is called *enthalpy*.

Now

$$\begin{aligned} dH &= dU + p dV + V dp \\ &= T dS - p dV + \mu dN + p dV + V dp \end{aligned}$$

or

$$\boxed{dH = T dS + V dp + \mu dN.}$$

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

$$dH = dU + d(pV)$$

and

$$dU = dQ - dW + \mu dN.$$

Again we partition the work into two components:

$$dW = p dV + dW_{\text{free}}.$$

Now

$$dH = dQ + V dp - dW_{\text{free}} + \mu dN$$

and for a finite process

$$\Delta H \leq \int T dS + \int V dp - \Delta W_{\text{free}} + \int \mu dN.$$

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

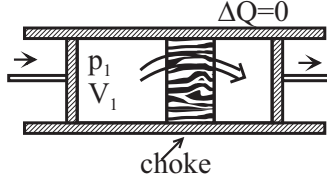
$$\Delta H \leq -\Delta W_{\text{free}}$$

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

Note: Another name of enthalpy is *heat function* (in constant pressure).

Joule-Thomson phenomenon

Flow of gas through a porous wall (“choke”):



p_1 and p_2 are constant (in time), $p_1 > p_2$ and the process irreversible. When a differential amount of matter passes through the choke the work done by the system is

$$dW = p_2 dV_2 + p_1 dV_1.$$

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

The work done by the system is

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

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*,

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

We consider now a *reversible* isenthalpic (and $dN = 0$) process $\text{init} \rightarrow \text{final}$. Here

$$dH = T dS + V dp = 0,$$

so

$$dS = -\frac{V}{T} dp. \quad (*)$$

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

$$dT = \left(\frac{\partial T}{\partial S}\right)_p dS + \left(\frac{\partial T}{\partial p}\right)_S dp.$$

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

$$dT = \frac{T}{C_p} dS + \frac{T}{C_p} \left(\frac{\partial V}{\partial T}\right)_p dp.$$

Substituting into this the differential dS 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.

2.4. Free energy

The Legendre transform

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

or

$$\boxed{F = U - TS}$$

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

Now

$$\boxed{dF = -S dT - p dV + \mu dN,}$$

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

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

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

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

From these we obtain the Maxwell relations

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

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

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

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; i.e. the control variables are T and V (typically at constant N). Very useful quantity in physics!

2.5. Gibbs free energy

The Legendre transformation

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

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

$$\boxed{G = U - TS + pV.}$$

Its differential is

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

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

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

when (T, p, N) is constant.

The Gibbs function is suitable for systems which are allowed to exchange mechanical energy and heat in heat- and pressure baths.

2.6. Grand potential

The Legendre transform

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

defines the *grand potential*

$$\boxed{\Omega = U - TS - \mu N.}$$

Its differential is

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

so the natural variables are T , p and μ .

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

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

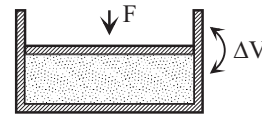
when (T, V, μ) is constant.

The grand potential is suitable for systems that are allowed to exchange heat and particles.

Bath

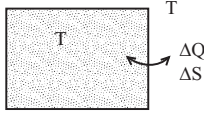
A *bath* is an equilibrium system, much larger than the system under consideration, which can exchange given extensive property with our system.

Pressure bath

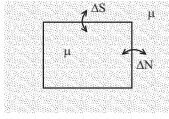


The exchanged property is the volume or a corresponding generalized displacement; for example magnetization in a magnetic field.

Heat bath



Particle bath



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

2.7. Thermodynamic response functions

Response functions are thermodynamic quantities most accessible to experiment. They give us information about how a specific state variable changes as other independent state variables are changed. They can be classified as *mechanical* (compressibility, susceptibility) and *thermal* (heat capacity) responses.

1) 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) Isothermal 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

Heat capacity C is a measure of the amount of heat needed to raise the temperature of a system by a given amount.

In a reversible process we have

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

The heat capacity C is defined so that

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

Keeping volume and N constant, we define

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

Now, according to the first law at constant N, V

$$dU = T dS - p dV + \mu dN = T dS.$$

Using $S = -(\partial F/\partial T)_{V,N}$, we can write

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N} = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_{V,N}$$

5) Isobaric heat capacity

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

Because

$$dH = T dS + V dp + \mu dN,$$

and using $S = -(\partial G/\partial T)_{p,N}$, one can write

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

Relating response functions

Now

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

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

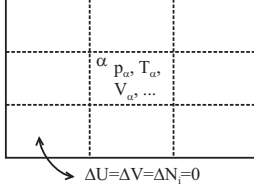
$$C_p = C_V + VT \frac{\alpha_p^2}{\kappa_T}.$$

Thus, $C_p > C_V$.

2.8. Thermodynamical equilibrium state

According to the 2nd law, the entropy of an isolated equilibrium system must be at maximum. Thus, any local fluctuation must cause the entropy to decrease; if it were not so, the system could move to a new higher entropy state, which cannot happen in an equilibrium system by definition.

We divide the system into fictitious 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 equilibrium the state variables are defined in each element, e.g.

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

and

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

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

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

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.

2.9. Stability conditions of matter

In a steady equilibrium the entropy has the true maximum so that small variations can only reduce the entropy.

We again consider an isolated system divided into parts, and 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 . In order to study the maximality of the entropy, the entropy of the partial system α , S_{α} , needs to be expanded into second order in $\{\Delta U_{\alpha}, \Delta V_{\alpha}, \Delta N_{j\alpha}\}$. We write S_{α} close to an equilibrium as the Taylor series

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

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

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

and similarly for other partial derivatives.

The 1st order differentials drop out, because $\sum_{\alpha} \Delta U_{\alpha} = 0$. Thus,

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

This can be rewritten as

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

Using the first law we get

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

This can be further written as

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

where

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

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

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

The condition $C_V \geq 0$ is a condition for thermal stability: if a small excess of heat energy is added to a volume element of fluid, the temperature of the volume element must increase.

The condition $\kappa_T \geq 0$ is a condition for mechanical stability: if a volume of a small fluid element (fixed N) increases, the pressure must go down, so that the larger pressure from the environment halts and reverses the growth.

Likewise $\frac{\partial \mu}{\partial N} \geq 0$ is a condition for chemical stability. Recall that

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_{V,N} = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_{V,N} > 0$$

Thus, F is a *concave* function of T .

Similarly,

$$\frac{1}{\kappa_T} = -V \left(\frac{\partial p}{\partial V} \right)_{T,N} = V \left(\frac{\partial^2 F}{\partial V^2} \right)_{T,N}$$

and F is a *convex* function of V .

3. Applications of thermodynamics

3.1. Classical ideal gas

For a full description of the thermodynamics of a system we need to know both the *equation of state* and some *thermodynamic potential*. EOS gives us mechanical response functions, but for thermal response functions we need also some potential.

From the ideal gas equation of state

$$pV = Nk_B T$$

we obtain directly the mechanical response functions

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

Thermal response functions cannot be derived from the equation of state. Empirically it has been observed

$$C_V = \frac{1}{2} f k_B N.$$

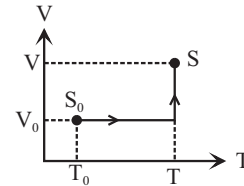
Here $\frac{1}{2} f k_B$ is the specific heat capacity/molecule and f is the number of degrees of freedom of the molecule.

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

For real gases $f = f(T, p)$, which is different from ideal gas because of internal degrees of freedom (vibrations), interactions between the molecules and quantum mechanical effects.

Entropy

Entropy can be obtained from thermal and mechanical response functions by integrating along the trajectory



The differential is

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

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 3rd law: $S \rightarrow -\infty$, when $T \rightarrow 0$. 3rd law relies on the quantum nature of real matter!

Internal energy

We substitute into the first law (N const.)

$$dU = T dS - p dV$$

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 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

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

If we choose $U_0 = C_V T_0$, we get for the internal energy

$$U = \frac{1}{2}fNk_B T.$$

Now

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

or

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

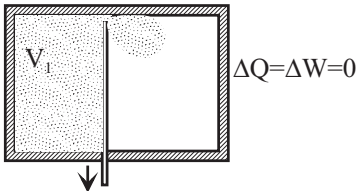
or

$$C_p = \gamma C_V,$$

where γ is the *adiabatic constant*

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

3.2. Free expansion of gas



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

a) Ideal gas

Now

$$U = \frac{1}{2}fk_B TN,$$

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

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

b) Real gas equation of state

The internal energy and the number of particles are constant:

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

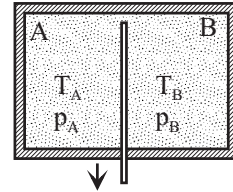
The *Joule coefficient* $\left(\frac{\partial T}{\partial V} \right)_{U,N}$ characterizes the behaviour of the gas during free expansion (cf. Joule-Thompson coefficient):

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

Note that this is differential form (∂V) ; with a finite process one must integrate over differential changes.

3.3. Mixing entropy

Consider different gases A and B, separated by a partition:



We assume that initially $p_A = p_B = p$ and $T_A = T_B = T$. The partition is removed and the gases mix. The process is irreversible 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

$$p = \sum_j p_j.$$

Method 1:

Each constituent gas expands to 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

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

Now $\Delta S_{\text{mix}} \geq 0$, since $0 \leq x_j \leq 1$.

Method 2:

For a process taking place in constant pressure and temperature the Gibbs function is the suitable potential:

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

where

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

Before mixing

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

and after mixing

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

so the change in the Gibbs function is

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

Because

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

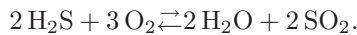
we get for the mixing entropy

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

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 reason is that in classical ensemble the particles are distinguishable, and mixing of A and B really happens. In quantum mechanics this apparent contradiction is removed by employing quantum statistics of identical particles.

3.4. Chemical reactions

Consider for example the chemical reaction



In general 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	H ₂ S	O ₂	H ₂ O	SO ₂
ν_j	-2	-3	2	2

We define the *degree of reaction* ξ so that

$$dN_j = \nu_j d\xi.$$

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

$$\xi \geq 0.$$

Let us assume that p and T remain constant during the reaction. Then a suitable potential is the Gibbs function

$$G = \sum_j \mu_j N_j.$$

Its differential is

$$dG = \sum_j \mu_j dN_j = d\xi \sum_j \nu_j \mu_j.$$

We define

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

$\Delta_r G$ is thus the change in the Gibbs function per one reaction (often called the affinity).

Since (p, T) is constant G has a minimum at equilibrium. The equilibrium condition is thus

$$\Delta_r G^{\text{eq}} = \sum_j \nu_j \mu_j^{\text{eq}} = 0.$$

In a nonequilibrium $dG/dt < 0$, so if $\Delta_r G > 0$ we must have $d\xi/dt < 0$, i.e. the reaction proceeds to left and vice versa. Let us 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 $p_j = x_j p$ is the partial pressure of component j and

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

So

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

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, which depends only on T . The equilibrium condition is historically called the *law of mass action*.

For the reaction above

$$\frac{x_C^2 x_D^2}{x_A^2 x_C^3} = pK(T).$$

The *heat of reaction* is the change of heat energy $\Delta_r Q$ per one reaction to right. A reaction is

- *Endothermic*, if $\Delta_r Q > 0$ i.e. the reaction takes heat.
- *Exothermic*, if $\Delta_r Q < 0$ i.e. the reaction releases heat.

We write $\Delta_r G$ as

$$\Delta_r G = -k_B T \ln K(T) + k_B T \sum_j \nu_j \ln p x_j.$$

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

$$dG = -S dT + V dp$$

holds in a reversible process and

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

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

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

Now

$$\frac{\partial}{\partial T} \left(\frac{\Delta_r G}{T} \right) = -k_B \frac{d}{dT} \ln K(T),$$

so that

$$\Delta_r H = k_B T^2 \frac{d}{dT} \ln K(T).$$

This expression is known as the *heat of reaction*.

3.5. Phase equilibrium

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

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

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

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

and the conditions (*) take the form

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

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.

3.6. Phase transitions

In a phase transition the chemical potential

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

is continuous. Instead

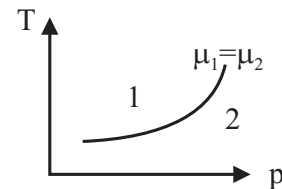
$$S = - \left(\frac{\partial G}{\partial T} \right)_p$$

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 1st order derivatives are continuous but 2nd order discontinuous. Otherwise the transition is *continuous*.



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

$$\Delta S = -\left(\frac{\partial G}{\partial T}\right)_p^{(2)} + \left(\frac{\partial G}{\partial T}\right)_p^{(1)}$$

$$\Delta V = \left(\frac{\partial G}{\partial p}\right)_T^{(2)} - \left(\frac{\partial G}{\partial p}\right)_T^{(1)}$$

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

$$\Delta Q = T \Delta S = \Delta U + p \Delta V = \Delta(U + pV)$$

$$= \Delta H.$$

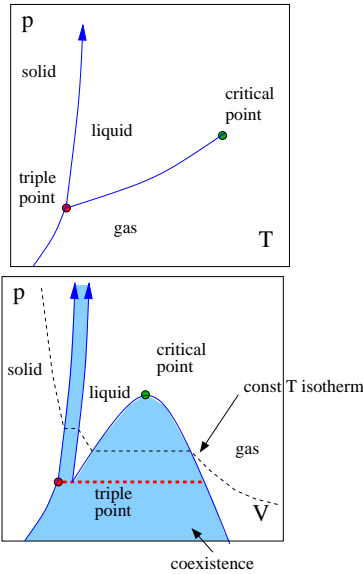
ΔQ is called the *phase transition heat* or the *latent heat*.

Note: First order transitions have non-zero latent heat but not the higher order ones.

Typical phase diagram of solid-liquid-gas -system: lines are 1st order transitions, critical point is 2nd order. (triple point is 1st order).

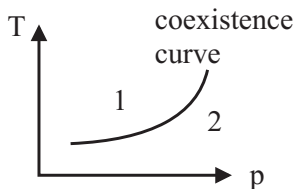
Water: $p_T = 610\text{Pa}$, $T_T = 0.01^\circ\text{C}$;

$p_c = 22\text{ MPa}$, $T_c = 374.15^\circ\text{C}$.



Because of phase *coexistence*, phase diagrams are simplest in “force”-type coordinates $(T, p, \mu, \bar{H}, \dots)$.

3.7. Phase coexistence



On the coexistence curve

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

and

$$dG = -S dT + V dp$$

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

$$G_1(p + dp, T + dT, N) = G_2(p + dp, T + dT, N),$$

so that

$$-S_1 dT + V_1 dp = -S_2 dT + V_2 dp$$

or on the curve

$$\frac{dp}{dT} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{\Delta S}{\Delta V} = \frac{T^{-1} \Delta H}{\Delta V}$$

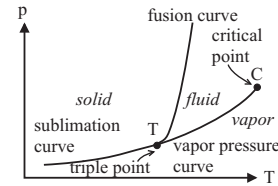
and we end up with the *Clausius-Clapeyron equation*

$$\left(\frac{dp}{dT}\right)_{\text{coex}} = \frac{1}{T} \frac{\Delta H}{\Delta V}.$$

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

Examples

a) Vapour pressure curve



We consider the transition

liquid \rightarrow vapour.

Assuming ideal gas we have

$$\Delta V = V_v = \frac{Nk_B T}{p},$$

because $V_{l(\text{iquid})} \ll V_{v(\text{apor})}$, and

$$\left(\frac{dp}{dT}\right)_{\text{coex}} = \frac{\Delta H_{lv} p}{Nk_B T^2}.$$

If the vapourization heat (the latent heat) ΔH_{lv} is roughly constant on the vapour pressure curve we can integrate

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

(this assumption is not true near crit. point!)

b) Fusion curve

Now

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

can be positive or negative (for example H_2O).

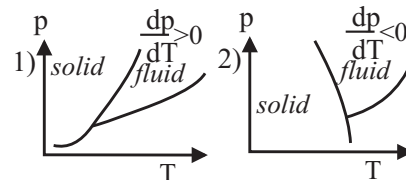
According to the Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta H_{ls}}{T \Delta V_{ls}}$$

we have

$$\frac{dp}{dT} > 0, \quad \text{if } \Delta V_{ls} > 0 \quad 1)$$

$$\frac{dp}{dT} < 0, \quad \text{if } \Delta V_{ls} < 0 \quad 2)$$



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

$$dH = T dS + V dp = C_p dT + V(1 - T\alpha_p) dp,$$

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

$$dS = \left(\frac{\partial S}{\partial p}\right)_T dp + \left(\frac{\partial S}{\partial T}\right)_p dT = -\left(\frac{\partial V}{\partial T}\right)_p dp + \frac{C_p}{T} dT.$$

The vapour pressure is small so $dp \approx 0$, and

$$H_s = H_s^0 + \int_0^T C_p^s dT \quad \text{solid phase}$$

$$H_v = H_v^0 + \int_0^T C_p^v dT \quad \text{vapour (gas).}$$

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

$$\Delta V_{vs} = \frac{Nk_B T}{p} - V_s \approx \frac{Nk_B T}{p},$$

so

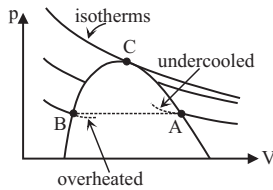
$$\frac{dp}{dT} = \frac{\Delta H_{vs}}{T \Delta V_{vs}} \approx \frac{p \Delta H_{vs}}{Nk_B T^2},$$

where $\Delta H_{vs} = H_s - H_v$. For a monatomic ideal gas $C_p = \frac{5}{2}k_B N$, and

$$\ln \frac{p}{p_0} = -\frac{\Delta H_{vs}^0}{Nk_B T} + \frac{5}{2} \ln T - \frac{1}{k_B N} \int \frac{\int_0^T C_p^s dT'}{T^2} dT + \text{constant}.$$

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

Coexistence range



Matter is mechanically stable only if $\frac{dV}{dp} < 0$. Thus the range of stability lies outside of the points A and B . Overheated liquid and undercooled vapour are metastable (supercooling, -heating).

According to the Gibbs-Duheim relation (consider dG !)

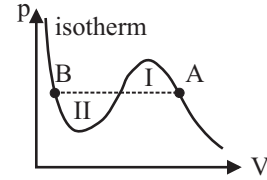
$$d\mu = -\frac{S}{N} dT + \frac{V}{N} dp$$

we have along isotherms

$$d\mu = \frac{V}{N} dp.$$

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

$$\mu_A - \mu_B = \int_A^B \frac{V}{N} dp = 0.$$



In many equations of state the phase transition happens when there is apparent instability $dp/dV > 0$ (for example, van der Waals). In this case, we can use *Maxwell's construction*: The points A and B have to be chosen so that the area I = area II.