4 Thermodynamics

As already mentioned in Chapter 1.3.1, thermodynamics (thermostatics would be a better name) describes macroscopical systems with the help of a few phenomenological rules which are called the laws of thermodynamics. These rules are not mathematically derived, but rather are generalisations or idealisations of experimental results. With this a big number of predictions become possible. The advantage of this is the generality of the predictions, the disadvantage is that material specific properties like the heat capacity of gases are not deducible.

4.1 Axiomatic Thermodynamic

Starting with the fundamental equation

$$U = TS - PV + \mu N \tag{4.1}$$

and taking the differential form

$$dU = TdS - PdV + \mu dN \tag{4.2}$$

$T(S,V,N)$, $P(S,V,N)$ and $\mu(S,V,N)$ can be derived, so $U(S,V,N)$ contains the complete information and everything can be derived from it. $T(S,V,N)$ does not contain all the informations since one would need the three functions $T(S,V,N)$, $P(S,V,N)$ and $\mu(S,V,N)$ to reconnect to $U(S,V,N)$ - they are the slopes of the 3-dimensional function F along the 3 directions. No one can do the Legendre transform.

$$F = U - TS \qquad\qquad\qquad = dU - TdS - SdT \tag{4.3}$$

$$= -SdT - PdV + \mu dN \tag{4.4}$$

$$dF(T,V,N) = -S(T,V,N)dT - P(T,V,N)dV + \mu(T,V,N)dN \tag{4.5}$$

So the above Legendre transform is performed by

- obtaining $S(T,V,N)$ by inversion of $T(S,V,N)$

- replacing S by $S(T,V,N)$ so that

$$F(T,V,N) = U(S,V,N) - TS \tag{4.6}$$

$$= U(S(T,V,N),V,N) - TS(T,V,N) \tag{4.7}$$

the inversions

In fact, By doing this $F(T,V,N)$ does indeed now contain the *also* complete thermodynamic information, so do $V(T,F,N)$, $T(F,V,N)$ and $N(F,T,V)$: *For example,* From the expression for dF, dV can be derived.

this differential the functions

$$dV = -\frac{S}{P}dT - \frac{1}{P}dF + \frac{\mu}{P}dN \qquad (4.8)$$

From these $\frac{S(T,F,N)}{P(T,F,N)}$, $P(T,F,N)$ and $\mu(T,F,N)$ can be obtained. There are many ways of formulating thermodynamics, but here the focus will lie only on the most important ones.

4.2 Equation of State and Response Functions

Here, again *We again consider the differential of F*

$$dF(T,V,N) = -S(T,V,N)dT - P(T,V,N)dV + \mu(T,V,N)dN \qquad (4.9)$$

where $F(T,V,N)$ contains the complete information, the functions $S(T,V,N)$, $P(T,V,N)$, $\mu(T,V,N)$ however do not. They contain other useful information though and so they are called equations of state and they are first derivatives of thermodynamic potentials. The following one is called the thermal equation of state.

The functions *are equivalent*

$$P(T,V,N) = -\frac{\partial F(T,V,N)}{\partial V} \qquad (4.10)$$

So $P(T,V,N)$, $V(P,T,N)$, $N(P,T,V)$, in fact $P(T,V,N) = P(T,v)$, where $v = \frac{V}{N}$. The so called caloric equation of state can be derived from

$$dU = TdS - PdV \mu dN \qquad (4.11)$$

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN \qquad (4.12)$$

$$\frac{\partial S(U,V,N)}{\partial U} = \frac{1}{T(U,V,N)}. \qquad (4.13)$$

(4.14)

$T(U,V,N)$ connects the variables T, U, V, N and is called Caloric equation of state.

From that $T(U,V,N)$ or $U(T,V,N)$ or others can easily be found. So in conclusion, first derivatives of thermodynamic potentials are called equations of state. Now one can also take the second derivatives. These give the so called response functions. Therefore here again is the thermal equation of state,

We *consider*

$$V(P,T,N) = \frac{\partial G(P,T,N)}{\partial P}. \qquad (4.15)$$

Typically one writes $U(T,V,N)$, which is derived by inversion.

G = U − TS + PV

Here ~~G~~ is the Gibbs free energy. ~~Now there are a lot of possibilities to take second derivatives. But~~ ~~starting from~~ *Considering* the total differential of $V(P,T,N)$ ~~this results in~~ *we obtain*

$$dV = \frac{\partial V}{\partial P}\Big|_{T,N}dP + \frac{\partial V}{\partial T}\Big|_{P,N}dT + \frac{\partial V}{\partial N}\Big|_{P,T}dN \tag{4.16}$$

So the second derivatives of thermodynamic potentials describe how state variables change, when other state variables are varied. These response functions are extremely important to characterise the system, so they are very useful in applications and hence they are tabulated in books. Now with this the isothermal compressibility κ_T can be written down as

$$\kappa_T(P,T) = -\frac{1}{V}\frac{\partial V(P,T,N)}{\partial P} \tag{4.17}$$

$$-V\kappa_T(P,T) = \frac{\partial V(P,T,N)}{\partial P} \tag{4.18}$$

$$= \frac{\partial^2 G(P,T,N)}{\partial P^2}. \tag{4.19}$$

Now the expansion coefficient α is

$$\alpha = \frac{1}{V}\frac{\partial V(P,T,N)}{\partial T} \tag{4.20}$$

$$= \alpha(P,T). \tag{4.21}$$

And the volume per particle is

$$\frac{\partial V(N,P,T)}{\partial N} = \frac{\partial Nv(P,T)}{\partial N} \tag{4.22}$$

$$= v(P,T) \tag{4.23}$$

With that equation (4.16) can be written as

$$dV = -V\kappa_T dP + V\alpha dT + vdN. \tag{4.24}$$

Hence differentials of equations of state define response functions.

4.3 Maxwell Relations

Again starting from the fundamental differential form $dU = TdS - PdV + \mu dN$:

$$T = \frac{\partial U(S,V,N)}{\partial S} \tag{4.25}$$

$$= T(S,V,N) \tag{4.26}$$

$$-P(S,V,N) = \frac{\partial U(S,V,N)}{\partial V} \tag{4.27}$$

So since *[handwritten: follows]*

$$\frac{\partial}{\partial V}\big|_{S,N}\frac{\partial U}{\partial S}\big|_{V,N} = \frac{\partial}{\partial S}\big|_{V,N}\frac{\partial U}{\partial V}\big|_{S,N} \tag{4.28}$$

it ~~is also true~~ that

[handwritten: can be confusing]

$$\frac{\partial T(S,V,N)}{\partial V} = -\frac{\partial P(S,V,N)}{\partial S}. \tag{4.29}$$

[handwritten: Maxwell relations]

This is called a Maxwell relation (not to be confused with Maxwell's equation from electrodynamics), which relates derivatives of state variables. This concept is a very powerful, but ~~confusing one~~, because there are many ~~of these equations~~. Just from U *[handwritten: (S,V,N)]* many pairs can be formed and there are many more:

$$F(T,V,N), G(T,P,N), H(S,P,N), \Omega(T,V,N)\ldots \tag{4.30}$$

4.4 Adiabatic Processes and the Application of Thermodynamic Calculus

The differential form of the first law of thermodynamics is (again)

$$TdS = dU + PdV - \mu dN \tag{4.31}$$

$$= \Delta Q \tag{4.32}$$

$$\neq dQ(!) \tag{4.33}$$

[handwritten: where in the last equation we want to stress that heat is not a potential.]

Adiabatic processes are processes where no heat is exchanged with the environment, for example by doing the process as quickly as possible, so nearly no heat can be conducted away from the system. To describe typical adiabatic processes, such as compression of a gas, it is ~~very wisely~~ to switch variables from U,V,N, for example to V,P,N or V,T,N. To make calculations easier, the μN in equation (4.31) is dropped, as N is constant most of the time anyway.

[handwritten: useful]

[handwritten: the is dependent of S]

4.4.1 ~~Now Going from~~ U,V ~~to~~ P,T

[handwritten: From $S(U,V)$ to $S(P,T)$ is written as and $S(V,T)$]

From the caloric equation of state ~~with $U(P,T)$,~~ dU ~~becomes~~

$$dU = \frac{\partial U}{\partial P}\big|_T dP + \frac{\partial U}{\partial T}\big|_P dT. \tag{4.34}$$

From the thermal equation of State $V(P,T)$ dV becomes

$$dV = \frac{\partial V}{\partial P}\big|_T dP + \frac{\partial V}{\partial T}\big|_P dT. \tag{4.35}$$

Deriving the Maxwell Relations

[handwritten: Energy]

[handwritten: We now want to relate the prefactors in Eq 4.36 & 4.37 to response function.]

$$dS = \frac{1}{T}\frac{\partial U}{\partial T}\Big|_V dT + \left(\frac{P}{T} + \frac{1}{T}\frac{\partial U}{\partial V}\Big|_T\right)dV \tag{4.52}$$

[handwritten: from]
$$\frac{\partial^2 S}{\partial T \partial V} = \frac{\partial^2 S}{\partial V \partial T} \qquad \text{we obtain} \tag{4.53}$$

$$\frac{\partial}{\partial V}\Big|_T \frac{1}{T}\frac{\partial U}{\partial T}\Big|_V = \frac{\partial}{\partial T}\Big|_V \left(\frac{P}{T} + \frac{1}{T}\frac{\partial U}{\partial V}\Big|_T\right) \tag{4.54}$$

$$\frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} = -\frac{1}{T^2}\left(P + \frac{\partial U}{\partial V}\Big|_T\right) + \frac{1}{T}\frac{\partial P}{\partial T}\Big|_V + \frac{1}{T}\frac{\partial^2 U}{\partial T \partial V} \tag{4.55}$$

$$P + \frac{\partial U}{\partial V}\Big|_T = T\frac{\partial P}{\partial T}\Big|_V \tag{4.56}$$

The second step now is to relate $\frac{\partial P}{\partial T}\big|_V$ to something already known.

[handwritten: derive this!! →]
$$dP = \frac{dV}{\frac{\partial V}{\partial P}\big|_T} - \frac{\frac{\partial V}{\partial T}\big|_P}{\frac{\partial V}{\partial P}\big|_T}dT \tag{4.57}$$

With that the derivative of P with respect to T can be rewritten as

$$\frac{\partial P}{\partial T}\Big|_V = -\frac{\frac{\partial V}{\partial T}\big|_P}{\frac{\partial V}{\partial P}\big|_T} \tag{4.58}$$

$$\frac{\partial P}{\partial T}\Big|_V = \frac{\partial P(T,V)}{\partial P(T,V)}\frac{\partial T}{\partial T}\Big|_V \tag{4.59}$$

$$= \frac{\partial P(U(T,V),V)}{\partial T} \tag{4.60}$$

$$= \frac{\partial P}{\partial U}\Big|_V \frac{\partial U}{\partial T}\Big|_V \qquad = \frac{\alpha}{\kappa_T} \tag{4.61}$$

With all of this

$$P + \frac{\partial U}{\partial V}\Big|_T = T\frac{\partial P}{\partial T}\Big|_V \tag{4.62}$$

$$= T \cdot \frac{\alpha}{\kappa_T} \qquad \text{[handwritten: } T\alpha \text{ over } \kappa_T\text{]} \tag{4.63}$$

Therefore

$$TdS = c_V dT + \frac{T\alpha}{\kappa_T}dV \tag{4.64}$$

$$TdS = c_P dT - \alpha TV dP \tag{4.65}$$

$$TdS = c_V \frac{\kappa_T}{\alpha}dP + \frac{c_P}{\alpha V}dV. \tag{4.66}$$

[handwritten: as an exercise]

Where the first one was derived above and the second ~~and third~~ are left for exercise. These *[handwritten: so-called]* new TdS equations are important since for adiabatic processes $TdS = 0$.

With those equation (4.31) becomes

Alternatively, we can write TdS in terms of dT and dV

$$TdS = \left[\frac{\partial U}{\partial P}\Big|_T + P\frac{\partial V}{\partial P}\Big|_T\right]dP + \left[\frac{\partial U}{\partial T}\Big|_P + P\frac{\partial V}{\partial T}\Big|_P\right]dT \tag{4.36}$$

~~This can sometimes be called the TdS equation. From $U(T,V)$ this becomes~~

$$TdS = \frac{\partial U}{\partial T}\Big|_V dT + \left[P + \frac{\partial U}{\partial V}\Big|_T\right]dV \tag{4.37}$$

The expansions 4.36 and 4.37 are the total differential of dS in terms of the ~~nor~~ non-canonical variables P,T and V,T. In contrast to dS in terms of U and V they do not contain the complete thermodynamical information.

Obtaining the Heat Capacity

The heat capacity is

from 4.37 and using that $\Delta Q = TdS$

$$C_V = \frac{\Delta Q}{\Delta T}\Big|_V \tag{4.38}$$

$$= \frac{\partial U}{\partial T}\Big|_V \tag{4.39}$$

from 4.36 and again using that $\Delta Q = TdS$

$$C_P = \frac{\Delta Q}{\Delta T}\Big|_P \tag{4.40}$$

$$= \frac{\partial U}{\partial T}\Big|_P + P\frac{\partial V}{\partial T}\Big|_P \tag{4.41}$$

$$= \frac{\partial(U + PV)}{\partial T}\Big|_P \tag{4.42}$$

$= U + PV$

$$= \frac{\partial H}{\partial T}\Big|_P \tag{4.43}$$

Here H is the enthalpy. For an ideal Gas $U = \frac{3}{2}k_B T N$ and hence

$$c_V = \frac{\partial U}{\partial T}\Big|_V \tag{4.44}$$

$$= \frac{3}{2}k_B N \tag{4.45}$$

$$c_P = \frac{\partial U}{\partial T}\Big|_P + P\frac{\partial V}{\partial T}\Big|_P \tag{4.46}$$

$$= \frac{3}{2}k_B N + Nk_B \tag{4.47}$$

$$= \frac{5}{2}Nk_B > c_V. \tag{4.48}$$

In deriving 4.47 we have used $\tag{4.49}$

~~So~~ the equation of state is

$$PV = Nk_B T \tag{4.50}$$

$$\frac{\partial V}{\partial T}\Big|_P = \frac{N_k B}{P} \quad \frac{Nk_B}{P} \tag{4.51}$$

So in general $c_P \geq c_V$, because part of ~~heat is connected~~ to mechanical work.

Converted

the absorbed

4.5 Different Ways of Expanding a Gas

These are many

Different paths of expanding a gas from an initial Volume V_i to a final volume $V_f > V_i$. The mechanical work W performed by the gas is
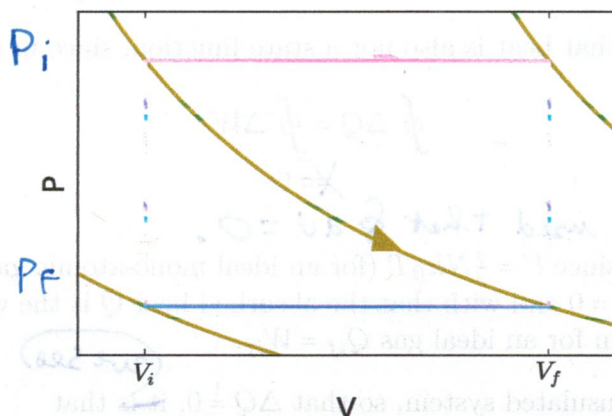
$$W = \int_{V_i}^{V_f} P(V)dV. \qquad (4.67)$$

Figure 4.1: $P-V$ diagram of an expanding gas from initial volume V_i to final volume V_f. Green lines are isotherms and blue lines are isochors. *or isobars*

Here it can be assumed that the state changes are slow, so that the equilibrium holds and $T(P,V)$ is given by the equation of state. So the path 1 can be assumed to be an isothermal expansion ($P = \frac{Nk_BT}{V}$). The work W^1 along this path is

$$W^1 = Nk_BT\ln\left(\frac{V_F}{V_i}\right) \qquad \leftarrow \text{derive} \qquad (4.68)$$

Obviously path 2 and 3 are not isothermal

$$W^2 = P_i(V_f - V_i) = \frac{Nk_BT}{V_i} = Nk_BT\left(\frac{V_f}{V_i} - 1\right) \qquad (4.69)$$

$$W^3 = P_f(V_f - V_i) = \frac{Nk_BT}{V_f} = Nk_BT\left(1 - \frac{V_i}{V_f}\right) \qquad (4.70)$$

Clearly $W^2 > W^1 > W^3$, since $\frac{V_f}{V_i} - 1 > \ln\left(\frac{V_f}{V_i}\right) > 1 - \frac{V_i}{V_f}$ since $x - 1 > \ln(x) > 1 - \frac{1}{x}$ for $x > 1$. The Work is not an exact differential, since $W_{i \to f}$ is path dependent. So the total Work W_{tot} done is *in a cyclic process is*

$$W_{\text{tot}} = \oint \Delta W \qquad (4.71)$$

$$= \oint PdV \qquad (4.72)$$

or

$$\neq 0 \qquad (4.73)$$

We clearly see that

65

a work function

this is the area of a cyclic process in the PV diagram, so the work done is not a state function. Because of that ~~statements like~~ $W(P,V)$ have no meaning.

4.5.1 Conclusions

closed contour

- Using a ~~path~~ integral over the first law of thermodynamics

$$dU = \Delta Q - \Delta W \tag{4.74}$$

it becomes clear that heat is also not a state function, since in general

$$\oint \Delta Q = \oint \Delta W \tag{4.75}$$

$$\cancel{\neq} 0. \tag{4.76}$$

Here we used that $\oint dU = 0$.

- In this example, since $U = \frac{3}{2} N k_B T$ (for an ideal mono-atomic gas) it also becomes clear that $U_f - U_i = 0$ and with that the absorbed heat Q is the work W performed along the isotherm for an ideal gas $Q_{if} = W_{if}$. *(we see)*

- For a thermally insulated system, so that $\Delta Q \overset{!}{=} 0$, ~~it is~~ that

$$dU = -\Delta W \tag{4.77}$$

$$= -dW \tag{4.78}$$

and the differential Work becomes an exact differential.

4.5.2 Adiabatic Expansion of an Ideal Gas

~~As a reminder,~~ the TdS equations ~~were~~ *are given Eq xy & yz*

$$TdS = c_V dT + \frac{T\alpha}{\kappa_T} dV \tag{4.79}$$

$$TdS = c_P dT - \alpha TV dP. \tag{4.80}$$

~~Also previously~~ *From Eq xy we obtain*

$$dT = \frac{1}{\alpha V} dV + \frac{\kappa_T}{\alpha} dP \tag{4.81}$$

So now equation (4.81) can be inserted into (4.79) and (4.80), which results in

$$TdS = \frac{c_V \kappa_T}{\alpha} dP + \frac{c_P}{\alpha V} dV. \tag{4.82}$$

← how? derive!

This now is the third TdS equation. It can be used to describe an adiabatic process ($TdS = 0$).

$$TdS = \frac{c_V \kappa_T}{\alpha} dP + \frac{c_P}{\alpha V} dV \qquad (4.83)$$

$$= 0 \qquad (4.84)$$

$$\qquad (4.85)$$

For the ideal gas we have

~~From that follows~~

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P}\Big|_T \qquad (4.86)$$

$$= -\frac{1}{V}\frac{\partial Nk_BT/P}{\partial P}\Big|_T \qquad (4.87)$$

$$= +\frac{Nk_BT}{VP^2} \qquad (4.88)$$

$$= \frac{1}{P}. \qquad (4.89)$$

For a monoatomic, ideal gas

$$c_V = \frac{3}{2}Nk_B \qquad (4.90)$$

$$c_P = \frac{5}{2}Nk_B \qquad (4.91)$$

Inserting these expressions into 4.85 we obtain

which are independent of V and P. ~~Because this is an adiabatic process,~~

$$\frac{dP}{P} = -\gamma\frac{dV}{V} \qquad (4.92)$$ *show derivation*

$$\frac{P_f}{P_i} = \left(\frac{V_i}{V_f}\right)^\gamma \qquad (4.93)$$

This now is the adiabatic equation and $\gamma = \frac{c_P}{c_V} \geq 1$ is the adiabatic exponent. Since $\gamma \geq 1$ the adiabatic $P(V)$ curves fall off faster than the isotherms. The temperature decreases during this adiabatic transformation. So γ is *for the ideal gas*

$$\gamma = \frac{c_P}{c_V} \qquad (4.94)$$

$$= \frac{5}{3} \qquad (4.95)$$

which can be used to describe the Carnot process.

4.6 Carnot Process

The Carnot process is the idealisation of real heat engines which convert heat into work. The $P-V$-diagram can be seen in figure 4.2.
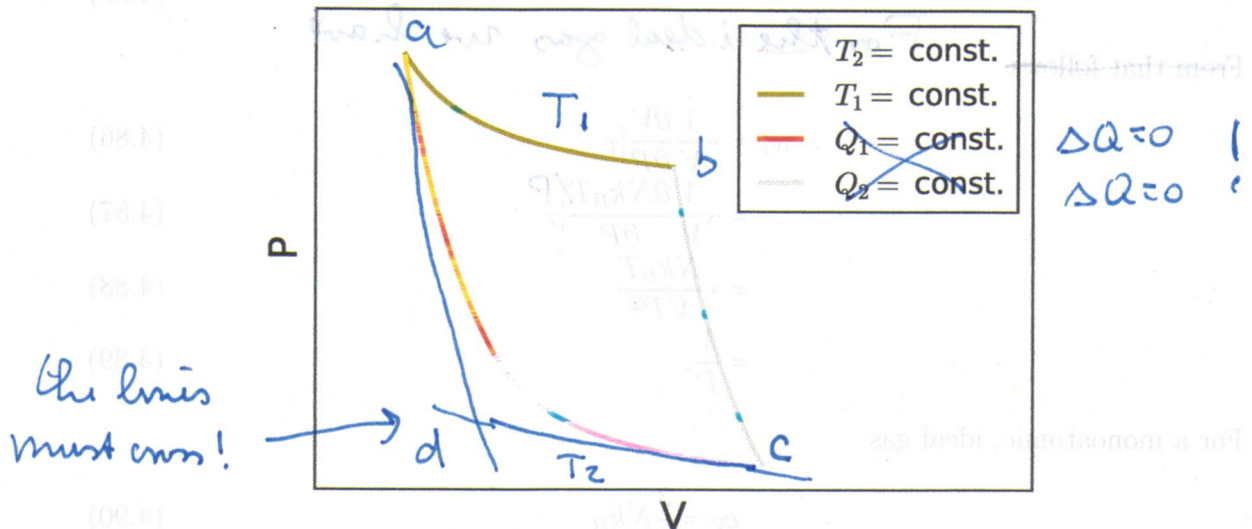

Figure 4.2: P-V-diagram of a typical heat engine / Carnot cycle

The cycle consist of four steps (colours refer to figure 4.2).

- $a \to b$: isothermal expansion at T_1 (green)
- $b \to c$: adiabatic expansion (light blue)
- $c \to d$: isothermal compression at $T_2 < T_1$ (blue)
- $d \to a$: adiabatic compression (red)

Figures 4.3 and 4.4 show these four steps again but ~~how it would look inside a real engine with cylinders.~~ Heat is transferred from a hot reservoir (T_1) to a cold reservoir (T_2).

As a result, in a semi-realistic realization with a cylinder that is periodically connected to two different heat reservoirs.
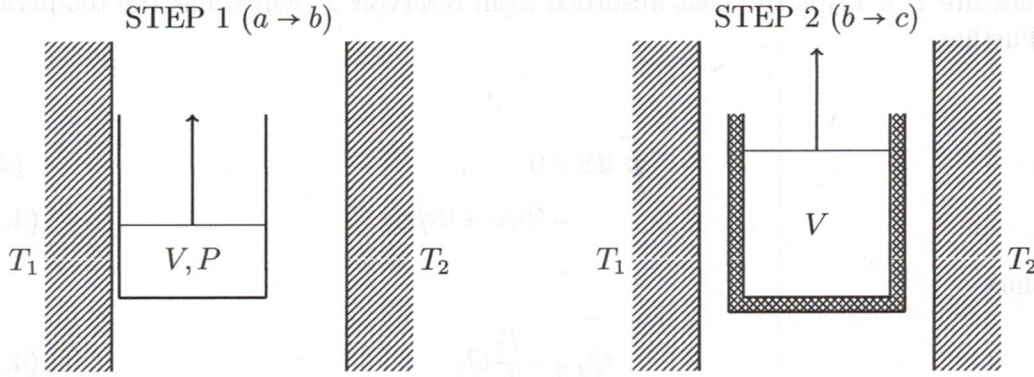
STEP 1 $(a \to b)$ STEP 2 $(b \to c)$

Figure 4.3: Carnot process steps 1 and 2: isothermal and adiabatic expansion. ~~Heat is transferred from a hot reservoir (T_1) to a cold reservoir (T_2)~~ (in step 2 the cylinder is thermally insulated - shown with the cross-hatching pattern).

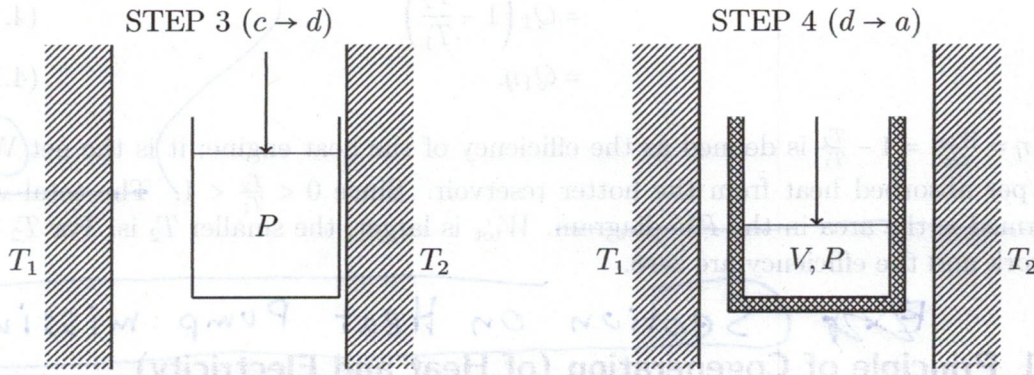STEP 3 $(c \to d)$ STEP 4 $(d \to a)$

Figure 4.4: Carnot process steps 3 and 4: isothermal and adiabatic compression. ~~Heat is transferred from a hot reservoir (T_1) to a cold reservoir (T_2)~~ (in step 4 the cylinder is thermally insulated - shown with the cross-hatching pattern)

As in every cycle the integral over U is zero

$$\oint dU = 0, \tag{4.96}$$

it follows that

$$\oint \Delta W \equiv W_{\text{tot}} \tag{4.97}$$

$$= Q_1 + Q_2. \tag{4.98}$$

In the adiabatic processes no heat is absorbed.

Here W_{tot} is the total work done by the system. This is equivalent to the area within one cycle in the $P-V$ diagram. Q_1 is the heat absorbed from reservoir 1 (which has the

temperature T_1). Q_2 is the heat absorbed from reservoir 2 (which has the temperature T_2). Further

$$\oint dS = 0 \tag{4.99}$$

$$= Q_1/T_1 + Q_2/T_2 \tag{4.100}$$

and thus

$$Q_2 = -\frac{T_2}{T_1}Q_1 \tag{4.101}$$

So heat is injected into the reservoir 2 and the total work W_{tot} is

$$W_{\text{tot}} = Q_1 - \frac{T_2}{T_1}Q_1 \qquad \text{we see that} \atop 0 < \eta < 1 \tag{4.102}$$

$$= Q_1\left(1 - \frac{T_2}{T_1}\right) \tag{4.103}$$

$$= Q_1\eta. \tag{4.104}$$

Here $\eta = \frac{W_{\text{tot}}}{Q_1} = 1 - \frac{T_2}{T_1}$ is defined as the efficiency of the heat engine; it is the net Work done per absorbed heat from the hotter reservoir. Since $0 < \frac{T_2}{T_1} < 1$. ~~The total work performed is the area in the PV-diagram.~~ W_{tot} is larger, the smaller T_2 is. For $T_2 = T_1$ the work and the efficiency are zero.

Ex2 (Section on Heat Pump missing!)

4.6.1 Principle of Cogeneration (of Heat and Electricity)

The idea is to heat a house as efficiently as possible. In the house is a tank with natural gas to burn and below the house ground water can be found. By just burning the gas per one Joule of burned gas the house is fed with (obviously) one Joule of heat. By using a Carnot engine this can be done much better: The first idea would be to just burn gas in a heat engine and use the electricity to power other appliances. The room is at $T_1 = 313K$ and the gas burns at $T_2 = 873K$. The efficiency of the heat engine is

$$\eta = 1 - \frac{313}{873} \qquad\qquad = 0.64 \tag{4.105}$$

So for every Joule of chemical energy $0.64J$ go into mechanical (quasi electrical) work and $0.36J$ go into the house. But this can be ~~done better:~~ *further improved* The $0.64J$ can be fed into the heat pump to transfer heat from the ground water at $283K$ to the house as well. The

coefficient of performance

~~efficiency~~ can be calculated via

$$\frac{1}{\eta} = \frac{T_1}{T_1 - T_2} \tag{4.106}$$

$$= \frac{313}{313 - 283} \tag{4.107}$$

$$= 10.4. \tag{4.108}$$

This means that for every one Joule of electric power 10.4 Joule of heat can be transferred. Using the $0.64\,J$ of electricity from above to power this ground-water-based heat engine

$$E = 0.36\,J + 10.4 \cdot 0.64\,J \tag{4.109}$$

energy conservation $\approx 6.7\,J$ *comes* $\tag{4.110}$

of heat can be transferred to the house per one Joule of burned gas. This seems like a violation of ~~the laws of thermodynamics~~, but it is not to forget that the groundwater actually became ~~a lot~~ colder by doing this. This is where the energy ~~came~~ from. There is just a huge amount of ground water, so the effect is not really noticeable. These systems are used in many private and public buildings. The process is called co-generation (of heat and electricity) (~~German: Kraft-Wärme-~~).

4.7 Transfer and Creation of Entropy

Now we discuss   *idealized*

Why real engines are less efficient than the ~~according~~ Carnot process. ΔQ is the heat transfer from reservoir 1 at T_1 to reservoir 2 at T_2. The two reservoirs are connected via a ~~heat sink.~~ *wire that conducts heat.*   *make a schematic figure!*

(is zero)

4.7.1 Reversible Case

The entropy changes in the reservoirs are

~~$T_1 = T_2$ with~~ $\Delta S_1 = -\frac{\Delta Q}{T_1} < 0$ and $\Delta S_2 = -\frac{\Delta Q}{T_2} > 0$. For $T_1 = T_2$ the total entropy change ~~is~~ $\Delta S_{\text{tot}} = \Delta S_1 + \Delta S_2 = 0$. This is an example of a reversible heat transfer. ~~Heat and entropy~~ *Heat is* ~~are transferred, so~~ the total entropy stays constant. The second law of thermodynamics allows these kinds of reversible processes to happen.

but

4.7.2 Irreversible Case

now we assume

~~In~~ opposite to the reversible case, ~~here~~ $T_1 > T_2$. The heat will flow from the hot to the cold reservoir. ΔQ is so small that T_1 and T_2 stay quasi constant. The entropy however

increases.

$$\Delta S_{\text{tot}} = \Delta S_1 + \Delta S_2 \tag{4.111}$$

$$= \Delta Q \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = \Delta Q \frac{T_1 - T_2}{T_1 T_2} \tag{4.112}$$

$$> 0 \tag{4.113}$$

And thus this process is irreversible. *Note that the opposite process, i.e. heat flowing from the cold to the hot reservoir, would increase the entropy and is not allowed. no heat leaks from the hot to the cold reservoir.*

4.7.3 Comments

- The Carnot process is reversible if ~~the mechanical energy is stored in between.~~
- The heat flow from the hot to the cold reservoir without the conversion to mechanical work is the main reason for the low efficiency of real heat engines.
- There is no heat engine with a higher efficiency than the Carnot engine.

4.8 ~~External~~ *Extremal* Properties of Thermodynamic Potentials

- In an insulated system the entropy $S(U, V, N)$ is maximised. *as shown in Section XY*
- If energy transfer is allowed between the small system and the reservoir,

$$dU = T dS - P dV + \mu dN \tag{4.114}$$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN \tag{4.115}$$

$$S_{\text{tot}} = S(U_1, V_1, N_1) + S(U - U_1, V - V_1, N - N_1) \tag{4.116}$$

$$= S(U_1, V_1, N_1) + S(U, V, N) - \frac{U_1}{T} \tag{4.117}$$

$$= S(U_1, V_1, N_1) - \frac{U_1}{T}. \quad = -\frac{1}{T}(U_1 - S_1 T) \tag{4.118}$$

$$\tag{4.119}$$

minimized!!

Schematic drawing!

$U_1 - TS_1$ is minimized

So from the second law of thermodynamics follows that $S_1 - \frac{U_1}{T}$ is maximised. So $T S_1 - U_1$ is maximised. The free entropy is ~~maximised~~ when T, V, N is fixed ~~and~~ $F_1 = U_1 - T S_1$ is ~~also maximised.~~   *$F = U_t - TS$*

- If entropy transfer and volume transfer are allowed, $G(P, T, N) = U - TS + PV$ is maximised. *Explain as in lecture!*

4.9 Thermodynamic Description of Phase Transitions

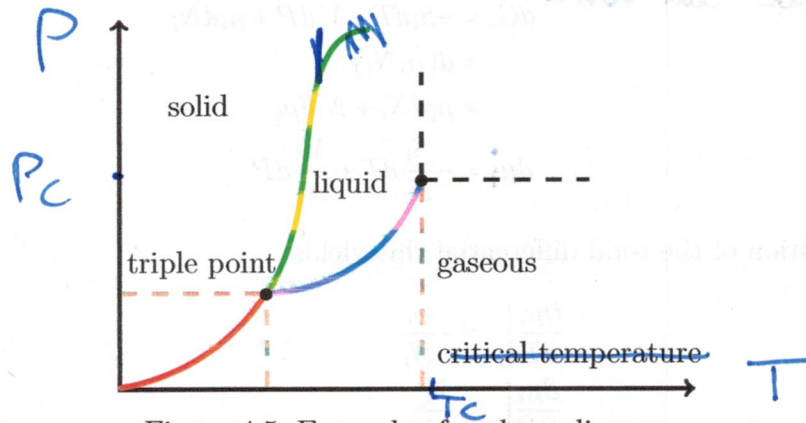Simple substances can exist in one of three phases, solid, liquid, vapour (gas).

Figure 4.5: Example of a phase diagram.

Along the lines in the diagram, two phases coexist, here are two solutions to the equation *(On these two-phase coexistence lines,)* of state with different volumes $v = \frac{V}{N}$ per particle. For a fixed P, the system splits into two coexisting phases (phase separation / phase equilibrium). At the triple point all three phases coexist. At the critical point the difference between two phases (liquid/vapour) vanishes.

4.9.1 Thermodynamic Stability at the Phase Transitions   *As shown in Section xy*

Consider a two phase system like liquid-vapour at constant T and P. At constant T,P, equilibrium is characterised by a minimum of the Gibbs free energy (free enthalpy)

$$G = U - TS + PV \tag{4.120}$$

$$= \sum_i \mu_i N_i \tag{4.121}$$

Now let $N = N_1 + N_2$, where N_1 is the number of particles in phase 1 and N_2 the number of particles in phase 2.

$$G = N_1\mu_1 + N_2\mu_2 \tag{4.122}$$

$$= N_1\mu_1 + (N - N_1)\mu_2 \tag{4.123}$$

This can be minimised with respect to N_1

$$\frac{\partial G}{\partial N_1} = \frac{\partial}{\partial N_1}(N_1\mu_1 + (N - N_1)\mu_2) \tag{4.124}$$

$$= \mu_1 - \mu_2 \tag{4.125}$$

$$\stackrel{!}{=} 0 \tag{4.126}$$

We see that in equilibrium,

The chemical potential has to be equal for the two phases.

4.9.2 Clausius-Clapeyron Equation

We consider two coexisting phases $i = 1, 2$.

For each phase ~~it is true, that~~ *we can write*

$$dG_i = -S_i dT + V_i dP + \mu_i dN_i \tag{4.127}$$

$$= d(\mu_i N_i) \tag{4.128}$$

$$= \mu_i dN_i + N_i d\mu_i \tag{4.129}$$

$$d\mu_i = -\frac{S_i}{N_i} dT + \frac{V_i}{N_i} dP \tag{4.130}$$

with the definition of the total differential this yields

$$\frac{\partial \mu_i}{\partial T}\bigg|_P = -\frac{S_i}{N_i} \tag{4.131}$$

$$\frac{\partial \mu_i}{\partial P}\bigg|_T = \frac{V_i}{N_i} \tag{4.132}$$

$$\frac{\partial(\mu_2 - \mu_1)}{\partial T}\bigg|_P = -\left(\frac{S_2}{N_2} - \frac{S_1}{N_1}\right) \tag{4.133}$$

$$= -\Delta s \qquad = -\Delta \Delta! \tag{4.134}$$

$$\frac{\partial(\mu_2 - \mu_1)}{\partial P}\bigg|_T = \frac{V_2}{N_2} - \frac{V_1}{N_1} \tag{4.135}$$

$$= \Delta v \tag{4.136}$$

where $s = \frac{S}{N}$ and $v = \frac{V}{N}$ are the entropy and the volume per particle.

with $\Delta \mu = \mu_2 - \mu_1$ this becomes

$$\Delta S = \frac{S_2}{N_2} - \frac{S_1}{N_1} \tag{4.137}$$

$$\Delta v = \frac{V_2}{N_2} - \frac{V_1}{N_1} \tag{4.138}$$

$$\frac{\frac{\partial \Delta \mu}{\partial T}\big|_P}{\frac{\partial \Delta \mu}{\partial P}\big|_T} = -\frac{\Delta s}{\Delta v} \tag{4.139}$$

where in the transformation we have used the differentiation chain rule Eq xy

$$\frac{dP_{co}(T)}{dT} = \frac{\partial P}{\partial T}\bigg|_{\Delta\mu = 0} \tag{4.140}$$

$$= \frac{\Delta s}{\Delta v} \tag{4.141}$$

With $\Delta q_i = T\Delta s$ which is the latent heat required for ~~vaporisation~~ *the phase change*, this becomes

$$\frac{dP_{co}}{dT}(T) = \frac{\Delta q_i}{T\Delta v} \tag{4.142}$$

This is the Clausius-Clapeyron equation.

consider melting transition of water and CO_2, show phase diagrams.