

2nd Law : Chapter 20

(19)

- most important part of thermodynamics
- connected with irreversibility (arrows of time)

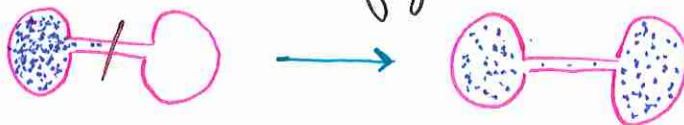
Exothermic \Rightarrow spontaneous ?

Not necessarily, even though products are lower in enthalpy.

spontaneous endothermic process : melting of ice above 0°C .

Spontaneous $\Delta H = 0$ process : expansion of gas into a vacuum

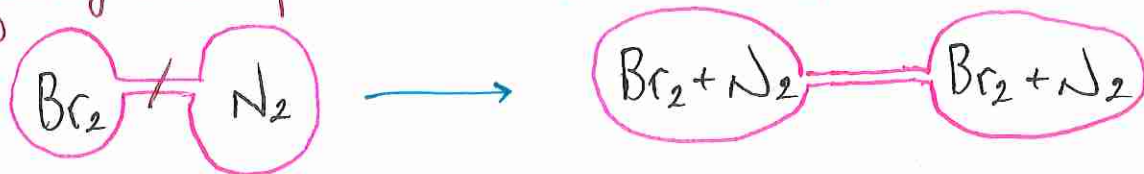
Fig 20.1



So the 1st law isn't the right tool to help with predicting whether a process will occur spontaneously or not.

Hint from gas example : maximize disorder

Fig 20.2

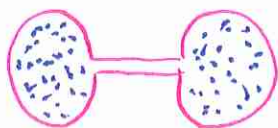


But probably shouldn't ignore enthalpy

preview : will result in $G = H - TS$ in Ch 22

First task : define a state function which quantifies disorder.

Microscopic connection :

Revisit the system :  = N molecules of an ideal gas ; each molecule is on L or R side (2 states).

Assume, for each molecule,
 $P(L) = P(R) = 1/2$

Then the equilibrium distribution
 is $N/2$ on L, $N/2$ on R

Why? Well, let us ask : what is the probability
 of a 1% deviation from equilibrium?

$\Omega = 2^N$ = number of possible states for the system

$$P(M \text{ on left}) = \frac{N!}{M!(N-M)!} \quad \text{Math chapter J}$$

Try it to see : $N=4$, $M=0$: 1 state (4 on right)

$M=1$: 4 states (any of 4 on left)

$M=2$: $\frac{4!}{2 \cdot 2} = 6$ states

$M=3$: 4 states (any of 4 on right)

$M=4$: 1 state (4 on left)

16 total = 2^4 .

For a 1% deviation look at

$$\frac{P(0.51 N \text{ on left})}{P(0.50 N \text{ on left})} = \frac{\frac{N!}{(0.51 N)! (0.49 N)!}}{\frac{N!}{(0.50 N)! (0.50 N)!}}$$

For $N=100$ this is $\frac{100!}{51!49!} / \frac{100!}{50!50!} = \frac{1}{51} \cdot \frac{50}{1} = 0.98$

For $N=1000$ this is $\frac{1000!}{510!490!} / \frac{1000!}{500!500!} = 0.82$

Need to use Stirling's approx: $\ln N! \approx N \ln N - N$ math chapter J

N	ratio
100	$50/51 = 0.98$
1000	0.82
10^4	0.136
10^{25}	2.1×10^{-9}
10^6	1.4×10^{-87}

out of one million molecules,
10 000 on "wrong" side

Notice that 10^6 molecules = 2×10^{-18} mol

Therefore we will never observe a 1% deviation for macroscopic systems

Define: $S = k_B \ln W$

W = number of microstates associated with a particular thermodynamic state

Maximizing disorder is equivalent to maximizing W since \log is monotone increasing.

Statement of 2nd Law :

$dS > 0$ for a spontaneous process in an isolated system

$dS = 0$ for a reversible process in an isolated system

Note: taking the system as everything gives

Fig 20.5

$\Delta S_{\text{universe}} \geq 0$ for spontaneous process

Section 20.9 (beyond us) shows that the molecular formula $S = k_B \ln W$ is equivalent to the thermodynamic formula $dS = \delta q_{\text{rev}} / T$.

Consider the heat transfer associated with a reversible small change in the T and V of an ideal gas.

$$\begin{aligned} \delta q_{\text{rev}} &= dU - \delta w_{\text{rev}} = C_V(T) dT + P dV \\ &= C_V(T) dT + \frac{nRT}{V} dV \end{aligned}$$

δq_{rev} is not a state function (we showed this in ch. 19)

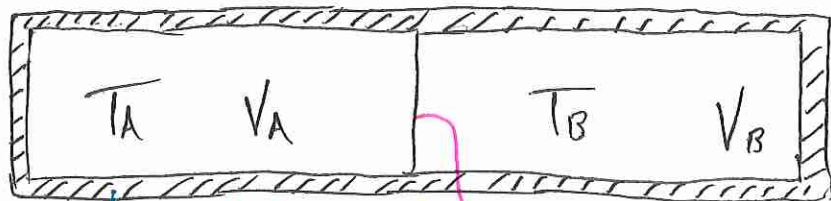
reason: RHS: T depends on V ; $\left(\frac{\partial C_V}{\partial V}\right)_T \neq \frac{\partial}{\partial T} \left(\frac{nRT}{V}\right)_V$

$$\frac{\delta q_{\text{rev}}}{T} = \frac{C_V(T) dT}{T} + \frac{nR}{V} dV \longrightarrow \text{state function}$$

Motivated by this, we define $dS = \delta q_{\text{rev}} / T$ and claim that it is a state function (in general, not just for ideal gases)

\rightarrow see problem 20.5

Fig 20.4



Note: This system will evolve in a way that is not reversible (assuming T_A and T_B are very different).

However we can use a reversible path to compute state functions if we want. How, then, you might ask, do a reversible and an irreversible process differ?

Answer: the way the surroundings change is different.

This concept can cause a lot of confusion.

$$U_A + U_B = \text{constant} \Rightarrow dU_A = -dU_B$$

$$V_A \text{ is constant ; } V_B \text{ is constant ; } S_{\text{sys}} = S_A + S_B$$

$$dU_A = \delta q_{\text{rev}} + \delta w_{\text{rev}} = T_A dS_A \quad (dV_A = 0)$$

$$dU_B = \delta q_{\text{rev}} + \delta w_{\text{rev}} = T_B dS_B \quad (dV_B = 0)$$

$$\Rightarrow dS = dU_B \left[\frac{1}{T_B} - \frac{1}{T_A} \right]$$

$T_B > T_A$: $dU_B < 0$ because we know heat will flow from the hot to the cold body.

$$\sum dS > 0$$

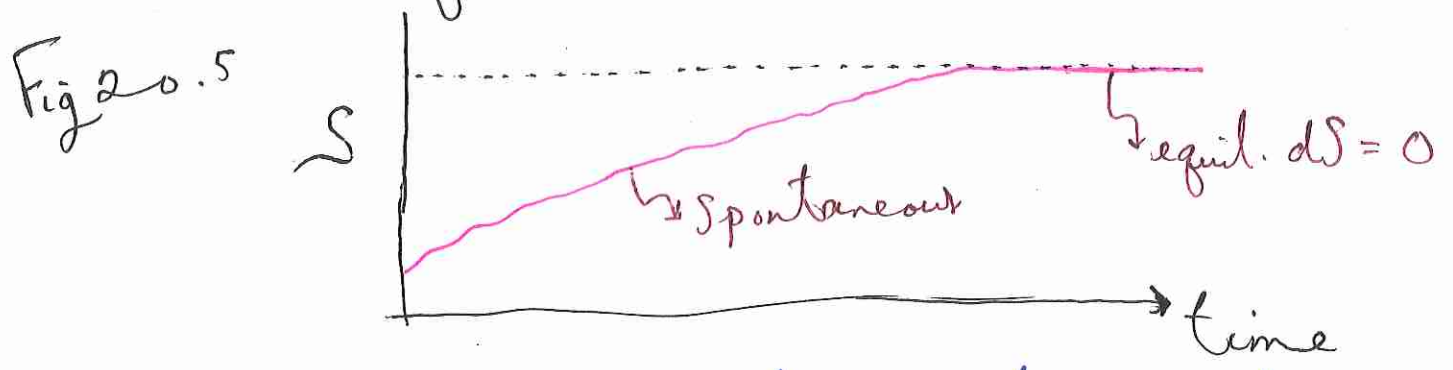
$$T_A > T_B : dU_B > 0, dS > 0$$

Conclusion: heat flow from hot \rightarrow cold body has $dS > 0$.

The advantage of this setup is that $dU = 0$ overall because the system was isolated.

For this restriction, $dS > 0 \iff \text{Spontaneous process}$

When is equilibrium reached?



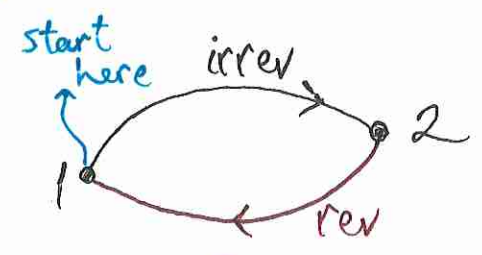
Also $dS = 0$ for a reversible process because the system remains essentially in equilibrium during the entire process.

One of the famous statements of the 2nd law:

Clausius Inequality: $\oint \frac{\delta q}{T} \leq 0$

for all thermodynamic cycles (system returns to its original state)

Consider the following cycle:

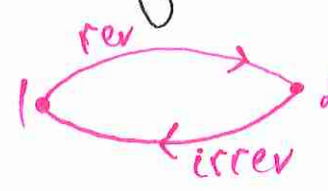


$$\oint \frac{\delta q}{T} = \int_1^2 \frac{\delta q}{T} + \int_2^1 \frac{\delta q_{rev}}{T} \leq 0$$

But $dS \equiv \frac{\delta q_{rev}}{T}$ so $\int_2^1 \frac{\delta q_{rev}}{T} = \int_2^1 dS = S_1 - S_2 = -\Delta S$

$$\Rightarrow -\Delta S + \int_1^2 \frac{\delta q}{T} \leq 0 \Rightarrow \int_1^2 \frac{\delta q}{T} \leq \Delta S \Rightarrow dS \geq \frac{\delta q}{T} \rightarrow \text{2nd Law}$$

Comment: We have to be careful because for a (25)
 "not nice" integral like $\int_1^2 \frac{\delta q}{T}$, the value of the
 integral depends on the path so we are not allowed to
 write $\int_1^2 \frac{\delta q}{T} = - \int_2^1 \frac{\delta q}{T}$ because this is only a property
 of exact differentials / state functions.

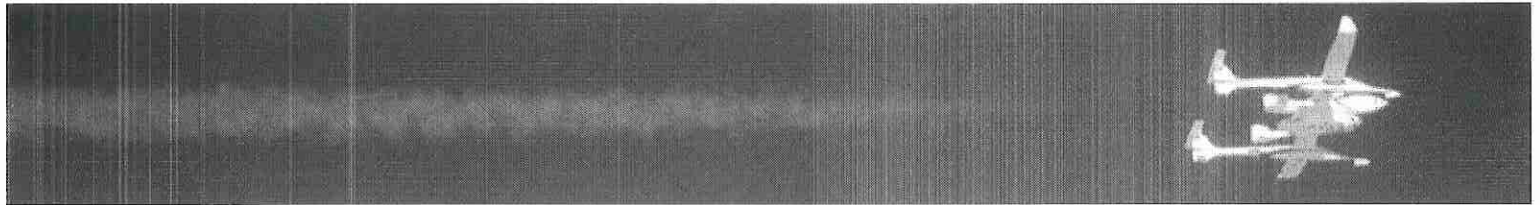
If we reverse things  $\int_1^2 \frac{\delta q_{rev}}{T} + \int_2^1 \frac{\delta q}{T} \leq 0$
 $\Rightarrow S_2 - S_1 + \int_2^1 \frac{\delta q}{T} \leq 0 \Rightarrow \int_2^1 \frac{\delta q}{T} \leq S_1 - S_2 = \Delta S \Rightarrow dS \geq \frac{\delta q}{T}$
 \hookrightarrow Since we are now going the other way

One way to think about/use this:
 Consider a cyclic process in which the system is isolated
 (no heat transfer to/from surroundings) and undergoes
 an irrev. process from $1 \rightarrow 2$, and then is allowed
 to interact with its surroundings as it is returned
 reversibly from $2 \rightarrow 1$.

We have $\Delta S \geq \int_1^2 \frac{\delta q_{irrev}}{T}$ from Clausius but

$\delta q_{irrev} = 0$ since isolated (adiabatic)

Thus $\Delta S \geq 0 \Rightarrow$ Entropy increases when an isolated
 system undergoes an irrev. process.



Thermodynamics and Propulsion

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3.1 Some Properties of Engineering Cycles; Work and Efficiency

As preparation for our discussion of cycles (and as a foreshadowing of the second law), we examine two types of processes that concern interactions between heat and work. The first of these represents the conversion of work into heat. The second, which is much more useful, concerns the conversion of heat into work. The question we will pose is how efficient can this conversion be in the two cases.

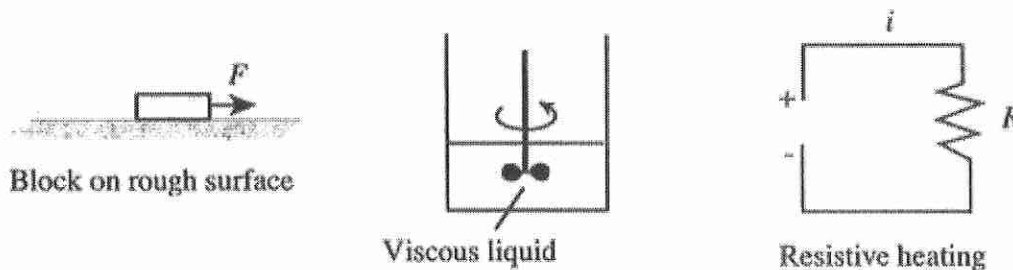


Figure 3.1: Examples of the conversion of work into heat

Three examples of the first process are given in Figure 3.1. The first is the pulling of a block on a rough horizontal surface by a force which moves through some distance. Friction resists the pulling. After the force has moved through the distance, it is removed. The block then has no kinetic energy and the same potential energy it had when the force started to act. If we measured the temperature of the block and the surface we would find that it was higher than when we started. (High temperatures can be reached if the velocities of pulling are high; this is the basis of inertia welding.) The work done to move the block has been converted totally to heat.

The second example concerns the stirring of a viscous liquid. There is work associated with the torque exerted on the shaft turning through an angle. When the stirring stops, the fluid comes to rest and there is (again) no change in kinetic or potential energy from the initial state. The fluid and the paddle wheels will be found to be hotter than when we started, however.

The final example is the passage of a current through a resistance. This is a case of electrical work being converted to heat, indeed it models operation of an electrical heater.

$$\text{Work during an isothermal expansion} = NRT \ln \left(\frac{P_1}{P_2} \right). \quad (3.2)$$

The lowest pressure to which we can expand and still receive work from the system is atmospheric pressure. Below this, we would have to do work on the system to pull the piston out further. There is thus a bound on the amount of work that can be obtained in the isothermal expansion; we cannot continue indefinitely. For a power or propulsion system, however, we would like a source of continuous power, in other words a device that would give power or propulsion as long as fuel was added to it. To do this, we need a series of processes where the system does not progress through a one-way transition from an initial state to a different final state, but rather cycles back to the initial state. What is looked for is in fact a **thermodynamic cycle** for the system.

We define several quantities for a cycle:

- Q_A is the heat absorbed by the system.
- Q_R is the heat rejected by the system.
- W is the net work done by the system.

The cycle returns to its initial state, so the overall energy change, ΔU , is zero. The net work done by the system is related to the **magnitudes** of the heat absorbed and the heat rejected by

$$W = \text{Net work} = Q_A - Q_R.$$

The thermal efficiency of the cycle is the ratio of the work done to the heat absorbed. (Efficiencies are often usefully portrayed as "What you get" versus "What you pay for." Here what we get is work and what we pay for is heat, or rather the fuel that generates the heat.) In terms of the heat absorbed and rejected, the thermal efficiency is

$$\eta = \text{thermal efficiency} = \frac{\text{Work done}}{\text{Heat absorbed}} = \frac{Q_A - Q_R}{Q_A} = 1 - \frac{Q_R}{Q_A}. \quad (3.3)$$

The thermal efficiency can only be 100% (complete conversion of heat into work) if $Q_R = 0$; a basic question is what is the maximum thermal efficiency for any arbitrary cycle? We examine this for several cases, including the Carnot cycle and the Brayton (or Joule) cycle, which is a model for the power cycle in a jet engine.

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UnifiedTP

Heat engines, refrigerators, and the 2nd Law.WORK \rightarrow HEAT?

Using friction, in a system in contact with a heat reservoir, work can be converted continuously into heat.

Since the reservoir is infinite, the system is always at temperature T . so U of system does not change.

$$\Rightarrow \delta q + \delta w = 0 \quad \text{or} \quad |q| = |w|.$$

$|w|$ is the work done on the system and $|q|$ is the heat rejected by the system at temp T to the reservoir.

HEAT \rightarrow WORK?

can we have 100% efficiency?

Yes if we use an isothermal reversible expansion from V_i to V_f ($V_f > V_i$)

$$1^{st} \text{ Law: } dU = \delta q + \delta w$$

For an ideal gas at constant T , $dU = 0 \Rightarrow q + w = 0$
 \Rightarrow all the heat absorbed is converted into work.

But the system is not in its initial state if work is done ($i \neq f$).

We want heat \rightarrow work to be continuous ($i = f$) and the system goes through a cycle so we can keep doing this).

$$1^{st} \text{ Law: } U = 0 \text{ for } i = f \text{ (cycle)} \Rightarrow q + w = 0.$$

Notation

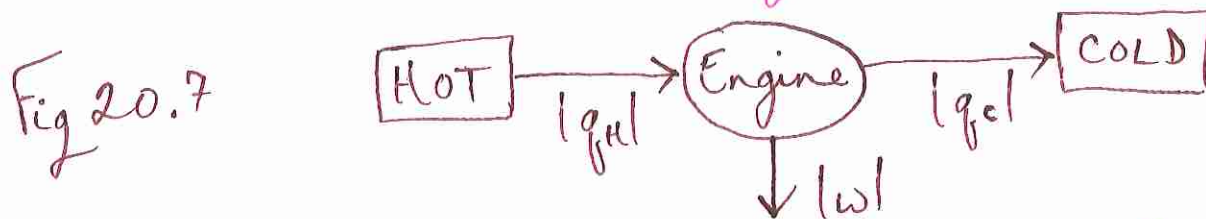
(27)

$|q_H|$: heat absorbed from hot reservoir

$|q_C|$: heat rejected to cold reservoir

$|w|$: work done on surroundings

the arrows will carry the sign information



$$|q_H| - |q_C| = |w| \quad \text{engine conserves } U \quad \text{continuous}$$

Obeying the first law does not preclude the conversion of heat into work, but the surroundings cannot be uniform (need different temp. reservoirs)

$$\text{Thermal efficiency} = \eta = \frac{\text{work output}}{\text{heat input}} = \frac{|w|}{|q_H|} = 1 - \frac{|q_C|}{|q_H|} < 1$$

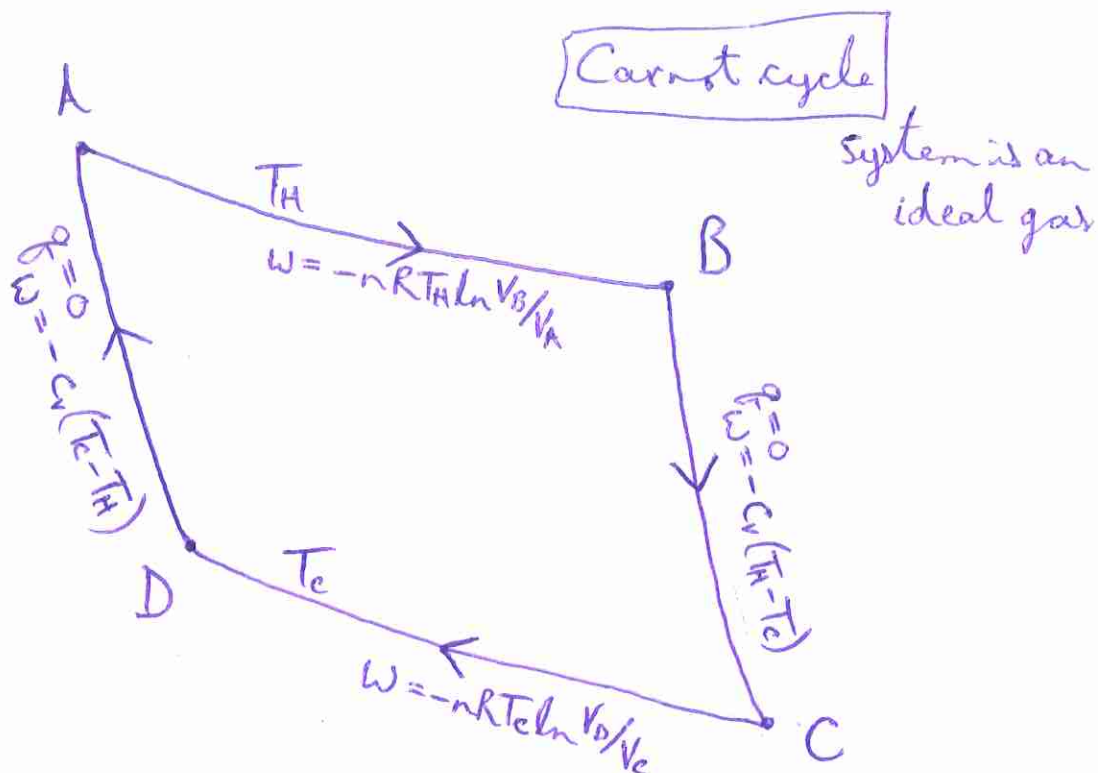
We know from ch. 19 that the maximum amount of work is obtained if the engine operates reversibly.

$$\text{In this case } \Delta S_{\text{engine}} = 0 = \frac{|q_H|}{T_H} - \frac{|q_C|}{T_C} \Rightarrow |q_C| = \frac{T_C}{T_H} |q_H|$$

$$\Rightarrow \eta = 1 - T_C/T_H < 1.$$

Realization of the maximum η : Carnot cycle

P



$D \rightarrow A$ adiabatic compression
 $A \rightarrow B$ isothermal expansion
 $B \rightarrow C$ adiabatic expansion
 $C \rightarrow D$ isothermal compression

} all reversible

V

$$\eta = \text{thermal efficiency} = \frac{|W|}{|q_H|} = 1 - \frac{|q_C|}{|q_H|}$$

$$\ln\left(\frac{V_A}{V_D}\right) = \ln\left(\frac{V_B}{V_C}\right)$$

For the Carnot cycle:

(28a)

$$|w| = nRT_H \ln V_B/V_A + nRT_C \ln V_D/V_C$$

$$|q_H| = nRT_H \ln V_B/V_A = \text{energy supplied as heat from the hot reservoir}$$

Need to work out the relationship between T and V for a reversible adiabatic process (section 19-5).

$$q=0 \Rightarrow dU = \delta w \quad \rightarrow \quad -PdV = -\frac{nRT}{V} dV$$

$$\frac{3}{2} nR dT = C_V(T) dT \quad \rightarrow \text{monoatomic ideal gas}$$

$$\Rightarrow \frac{3R}{2T} dT = -\frac{R}{V} dV \quad \text{divide both sides by } nT$$

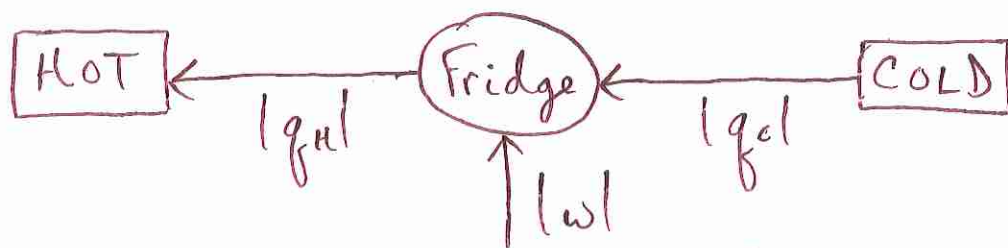
$$\Rightarrow \int_{T_1}^{T_2} \frac{3R}{2T} dT = -\int_{V_1}^{V_2} \frac{R}{V} dV \Rightarrow \frac{3}{2} \ln T_2/T_1 = \ln V_1/V_2$$

$$\text{Therefore } \ln V_A/V_D = \ln V_B/V_C \Rightarrow \ln V_A - \ln V_D = \ln V_B - \ln V_C$$

$$\Rightarrow -\ln V_D/V_C = \ln V_B/V_A$$

$$\text{Thus } \frac{|w|}{|q_H|} = \eta = 1 + \frac{T_C}{T_H} \frac{\ln V_D/V_C}{\ln V_B/V_A} = 1 - T_C/T_H.$$

Refrigerator: just a heat engine operating in reverse. (29)



work is always needed to transfer heat from a cold to a hot reservoir.

coefficient of performance = $\Omega = \frac{\text{heat extracted from cold}}{\text{work done}}$

$$\Omega = \frac{|q_C|}{|w|} = \frac{|q_C|}{|q_H| - |q_C|} > 1.$$

$$\text{Maximum performance } \Omega = \frac{T_C}{T_H - T_C} > 1.$$

→ Clausius statement of 2nd Law:

No process is possible whose sole result is the transfer of heat from a cooler to a hotter body.

Go back to Fig 20.1 and Fig 20.2 to examine the entropy change.

29a

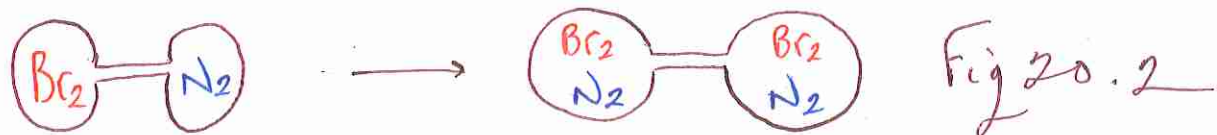
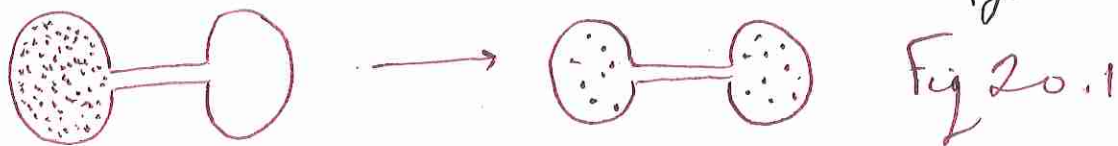


Fig 20.1 : irreversible adiabatic expansion into vacuum.

$$\Delta U = q + w \quad \text{but } q = 0 \text{ and } w = 0 !$$

Therefore T does not change since $U = \frac{3}{2} RT$.

Now, to calculate ΔS we need a reversible path.

We can write $\delta q_{\text{rev}} = -\delta w_{\text{rev}}$ at constant T (isothermal)

$$\text{and } \delta w_{\text{rev}} = -P dV = -\frac{nRT}{V} dV$$

$$\Rightarrow \Delta S = \int_1^2 \frac{\delta q_{\text{rev}}}{T} = - \int_1^2 \frac{\delta w_{\text{rev}}}{T} = nR \int_{V_1}^{V_2} \frac{dV}{V} = nR \ln V_2/V_1$$

What is the difference between the reversible and irreversible paths?

Answer: the difference is in the surroundings!

In both cases $\Delta S = \Delta S_{\text{sys}} = nR \ln V_2/V_1$.

For the irrev. process $\Delta S_{\text{surr}} = 0$ because there is no interaction between the system

and the surroundings
For a heat reservoir, because the temperature is uniform there is no heat transfer across a finite temperature difference and thus the heat exchange is reversible. Thus

Thus $\Delta S_{\text{TOT}} = 0$ for the reversible process $dS = \frac{\delta q_{\text{rev}}}{T} \Rightarrow \Delta S = q/T$

Why do we have the formula $\Delta S_{\text{sur}} = q_{\text{sur}}/T$ (29/6)
regardless of whether the change in the
system is reversible?

Atkins: S_{sur} is extensive that they remain at
constant pressure regardless of any events
taking place in the system, so $q_{\text{sur}} = \Delta H_{\text{sur}}$
and H is a state function so path independent

Engel/Reid: For a thermal reservoir at temp T ,
the mass of the reservoir is so large that its
temp. is only changed by an infinitesimal amount
 dT when heat is transferred between the
system and its surroundings. Therefore the
 S_{sur} always remain in internal equilibrium
during heat transfer.

Fig 20.2 : entropy of mixing

(29c)

Each gas is ideal and thus independent of the other. Thus each gas can be considered to expand from V_i to V_f .

$$\Delta S_{N_2} = n_{N_2} R \ln \frac{V_{TOT}}{V_{N_2}} = -n_{N_2} R \ln V_{N_2}/V_{TOT}$$

$$\Delta S_{Br_2} = n_{Br_2} R \ln V_{TOT}/V_{Br_2} = -n_{Br_2} R \ln V_{Br_2}/V_{TOT}$$

$$\Delta S_{mix} = \Delta S_{N_2} + \Delta S_{Br_2} = -n_{N_2} R \ln V_{N_2}/V_{TOT} - n_{Br_2} R \ln V_{Br_2}/V_{TOT}$$

Now assume $P_{N_2} = P_{Br_2} = P_{TOT}$ and that T is also constant.

In this case

$$\frac{V_{N_2}}{V_{TOT}} = \frac{n_{N_2} RT}{P_{N_2}} \cdot \frac{P_{TOT}}{n_{TOT} RT} = n_{N_2}/n_{TOT}$$

In other words $V \propto n$ for an ideal gas at constant T, P .

$$\Rightarrow \Delta S_{mix} = -n_{N_2} R \ln n_{N_2}/n_{TOT} - n_{Br_2} R \ln n_{Br_2}/n_{TOT}$$

Divide both sides by $R \cdot n_{TOT}$:

$$\Delta \bar{S}_{mix}/R = -x_{N_2} \ln x_{N_2} - x_{Br_2} \ln x_{Br_2} > 0.$$

where $x_{N_2} = \frac{n_{N_2}}{n_{TOT}}$ = mole fraction of N_2 .

Gibbs Paradox: take $n_{N_2} = n_{Br_2} = \frac{1}{2} n_{TOT}$ ($V_{N_2} = V_{Br_2} = \frac{1}{2} V_{TOT}$)

and replace the Br_2 gas with N_2 .

$$\text{Then } \Delta \bar{S}_{mix}/R = -\ln \frac{1}{2} = \ln 2 = 0.693.$$

But is there really any difference before and after "mixing"?