

Homework: See website.

22.1 Heat Engines and the Second Law of Thermodynamics, 2

22.2 A Heat Pump or Refrigerator 3

22.3 Reversible and Irreversible Processes. Probability and Entropy, 4

22.4 The Carnot engine, 5

22.4a Problem: A Carnot engine between 500 and 50 C, 7

22.4b In a gasoline engine (Otto engine), 8

22.5 Entropy, 9

22.5b (22.8) Macrostates and Microstates, 10

22.6 Macroscopic Entropy Definition, 12

22.7 Entropy Change for a Quasi Static Reversible Process of an Ideal Gas, 13

22.7a Entropy Changes During Phase Changes, 14

22.7b The entropy change during a thermal conduction, 15

22.7c Entropy Change in Calorimetric Processes, 15

Optional:

22.8 Thermodynamic Equilibrium (Enthalpie etc.), 18

22.9 Calculating the critical temperature of a real gas 19.

22.1 Heat Engines and the Second Law of Thermodynamics.

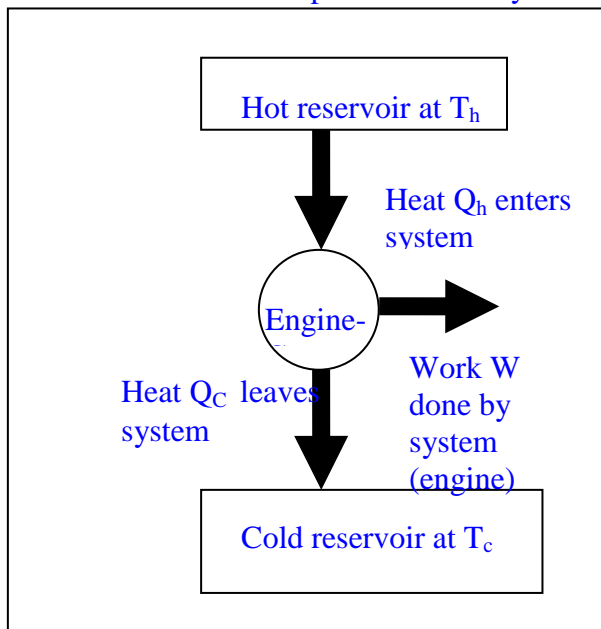
(22.1) Heat is the energy of a disordered movement of molecules.
 In a heat engine we attempt to turn the disordered movement into a ordered movements which can be used to do work on a continous, cyclical basis.

The ocean is a huge heat reservoir, in some areas with water temperatures of 25 degree Celsius. Wouldn't it be nice to build a ship with an engine that takes hot water out of the ocean, extracts work from it, during which process the water cools down. It seems reasonable to think that the energy difference $Q = mc\Delta T$ could be turned into work. Such a ship could run on hot water so to speak and leave a trail of ice behind it. Even though this sounds plausible, it cannot be done. The crucial point in this example is that we would have a machine which runs on the extraction of energy from a single heat reservoir, the ocean. Its cycle would start and end in the same heat reservoir. (This is called a perpetual machine of the second kind. BTW, a perpetual machine of the first kind would run, do work, without extracting energy from anything in the world.)

The statement that we cannot build a perpetual motion machine of the second kind is the essence of the second law of thermodynamics.

There are more sophisticated ways to say the same thing, some of these ways we are going to examine in more detail.

A heat engine carries some working substance (gasoline vapor-air mixture, steam) through a cyclic process during which (1) the working substance absorbs heat Q_h from a high-temperature energy reservoir (exploded gasoline-vapor-air mixture, hot steam), (2) work is done by the engine (exploding gas pushes piston), and (3) energy is expelled by heat Q_c to a different reservoir at a lower temperature. This cycle is continuously being repeated.



The system to which we apply our thermodynamic variables is a gas, which undergoes a **cyclical process**, forms a closed loop in the PV-space. The change in internal energy ΔU is therefore 0.

The heat exchange consists of stage (1) and (2). In stage (1) heat Q_h enters the system at the higher temperature T_h , and heat Q_c leaves the system at T_c . Work is done by the system (engine), therefore W_{eng} is negative. We indicate that by using $-W_{eng}$.

$$(22.2) \quad \Delta U = 0 = |Q_h| - |Q_c| - W_{eng}$$

$$(22.3) \quad W_{eng} = |Q_h| - |Q_c|$$

The thermal efficiency e is the ratio of the work to the heat input, it is the ratio of the work you get to the energy you pay for:

$$(22.4) \quad e = \frac{W_{eng}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|}$$

This leads to a second way of stating the second law of thermodynamics:

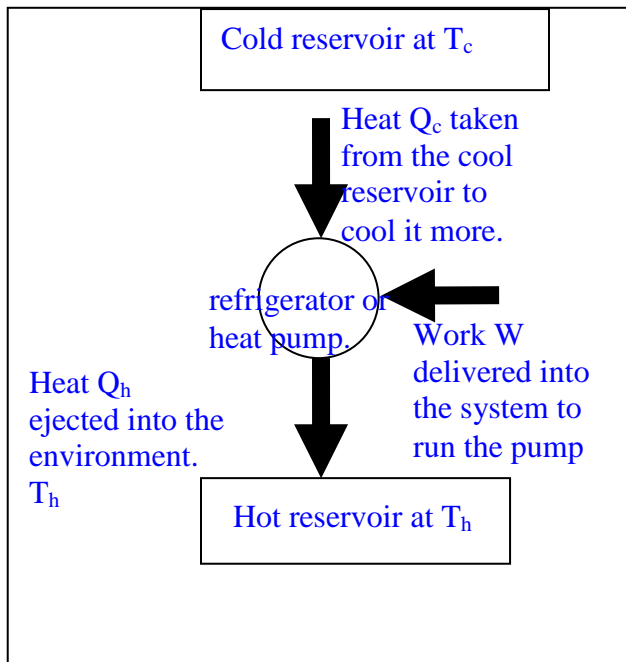
(22.5) **The thermal efficiency of a heat engine is always smaller than 1.**

Example:

The human body can be modeled as a heat engine to some degree, burning carbohydrates and fat and producing heat, energy, water and carbon dioxide in complex chemical reactions. These reactions require **catalysts** or **enzymes** to occur at low temperatures, around 40 °C. A typical sugar has an energy content of about 5000 cal/g. Let us assume that the human body has an efficiency of 0.1. How much work can the body do with 1 gram of sugar? How much unusable energy is produced?

$$(22.6) \quad e = \frac{W_{eng}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 0.1$$

The body can do 500 cal or 2009 J of work. It can lift 1kg through a vertical distance of 200 m. 4500 cal cannot be used for doing work.



22.2 A Heat Pump or Refrigerator,

serves to cool down a heat reservoir. Heat (hot air) Q_c is taken out of the cooler reservoir and ejected into the warmer reservoir as Q_h . To perform this cycle the necessary work-energy is delivered to the system, for example through the electricity running a refrigerator. **This means that W is positive.** We see that such a device is essentially the reverse process of a heat engine, in which work is being generated. (The book by Serway labels the heat amounts differently, be careful.)

$$(22.7) \quad \Delta U = 0 = |Q_c| - |Q_h| + W \Rightarrow W = |Q_h| - |Q_c|$$

The coefficient of performance COP (in cooling mode) is defined as the ratio of heat taken out of the cold reservoir (the fridge) and the work necessary to do this (what you pay for.)

$$(22.8) \quad COP(\text{in cooling mode}) = \frac{|Q_c|}{W}$$

Thus, we see that it is impossible to construct a cyclical machine whose sole effect is to transfer energy continuously by heat from a cooler object to another warmer object without the input of energy (for example electricity) or work.

Note: An important aspect of all heat transfer is that huge numbers of molecules are involved. In order to be able to talk about temperature these molecules must be in thermal equilibrium. Remembering Maxwell's distribution curves, we see that all of these processes are of a statistical nature.

Problem: A certain refrigerator runs at 0.50 kW and has a COP of 5.00. 3.0 liters of water at 20 degree Celsius are placed into the freezing department. How long does it take until the water has obtained a temperature of 10 degree Celsius below freezing?

The amount of heat extracted from the water is the heat to lower the water temperature to freezing, then the latent heat of melting, and then the energy to lower the temperature of ice from 0 to -10 degree Celsius. The heat capacity of water is 1.0 cal/gC. The latent heat of melting is 80 cal. The heat capacity of ice is 0.50 cal/gC. Therefore the total heat that must be extracted is:

$$Q_c = 3000g \cdot (1.00 \frac{\text{cal}}{\text{gC}^\circ} 20\text{C}^\circ + 80 \frac{\text{cal}}{\text{g}} + 0.50 \frac{\text{cal}}{\text{gC}^\circ} 10\text{C}^\circ) = 315\text{kCal} = 315 \cdot 4.186\text{kJ} = 1.32 \cdot 10^6 J$$

The refrigerator runs at 500 Watts.

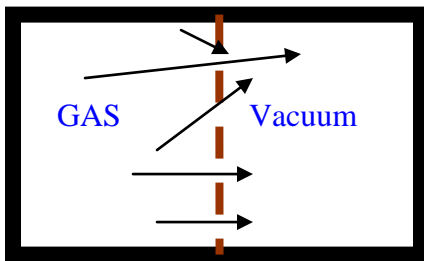
$$\text{Power} = \frac{\text{energy}}{\text{time}} = \frac{Q_c}{\Delta t}$$

Therefore: $\Delta t = \frac{Q_c}{P} = 2640 \text{ seconds} = 44 \text{ minutes}$. **What is wrong with this?**

The power rating refers to the energy input into the fridge not to the heat extracted. We must use $\text{COP} = Q_c/W$, or $W = Q_c/5$. The time required is therefore $44/5 \text{ minutes} = 8.8 \text{ minutes}$.

22.3 Reversible and Irreversible Processes. Probability and Entropy.

If you would look at a film showing two containers connected by a membrane, in which the gas would flow in such a way that it collects in one container and leaves the other empty, you would immediately know that the film is running backwards. Processes which, if left to themselves can only unfold in one direction, are called irreversible.



If there are only two gas molecules we know that it is possible that both molecules are in one and the same container. We just know that this is less likely, less probable. The more molecules we have, the less probable it is that all molecules assemble in one container.

If we call any situation in which we have certain amounts of molecules in both containers a state, we can say: **A state in which we have an approximately equal number of molecules in each container is more likely than a state in which there are many more molecules in one container than in the other.**

Or, put differently: *It is more probable that a state with an uneven distribution of molecules unfolds in a direction in which we have an even distribution of molecules, than the other way around.*

Or, the “natural” free movement of states is towards states of higher probability. If we replace the word probability in this sentence by entropy (S), we have a working definition of this important term. **the “natural” free movement of states is towards states of higher entropy S.** (This is yet another form of the second law of thermodynamics.)

All macroscopic processes are irreversible, they occur in the direction of higher probability (entropy) of states. $\Delta S > 0$ Reversible processes are characterised by no change in their entropy. $\Delta S = 0$ The entropy increases in all irreversible processes ($\Delta S > 0$).

22.4 The Carnot engine (see figure) is a (theoretical) cyclical series of **reversible processes**, which allow us to calculate the absolute highest “theoretical” efficiency of a heat engine. “Theoretical” here means an idealized situation which can never be achieved in reality. Another statement for the second law would be that a Carnot engine efficiency is impossible to achieve with a real engine. Carnot chose this particular cycle because we can calculate the work and heat exchange during each portion of the cycle. Each step of this cycle can be rendered infinitesimal, quasistatic. We know the laws for heat exchange in adiabatic and in isothermal processes.

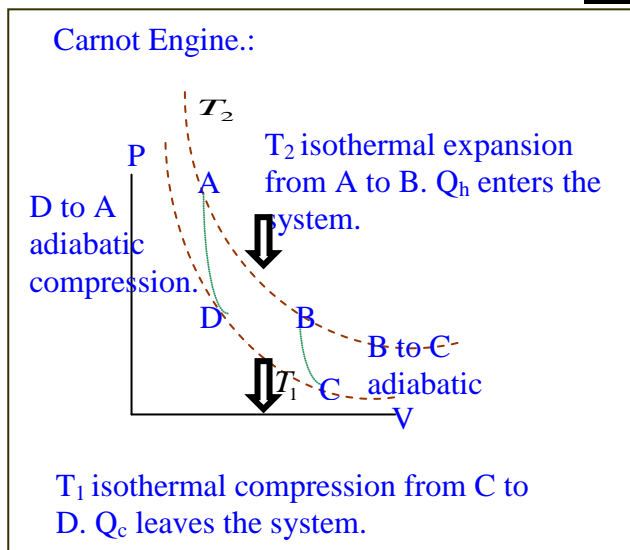
adiabatic: $PV^\gamma = \text{constant}$ or $TV^{\gamma-1} = \text{constant}$

(22.9) isothermal: $W = nRT \ln \frac{V_i}{V_f}$

For the efficiency we have from (22.4)

(22.10)

$$e = 1 - \frac{|Q_c|}{|Q_h|}$$



For the whole cycle we have $\Delta U = 0$ and according the second law: $W_{eng} = |Q_h| - |Q_c|$

For the adiabatic branches we have

$$\Delta U = \frac{3}{2} nR\Delta T$$

where we remember that the

internal energy change is completely calculated through the temperature change.

The work done on the system is equal to negative the work done by the engine, which is the difference between the absolute values of Q_h and Q_c .

Note that the adiabatic lines ($PV^\gamma = \text{constant}$) in a PV diagram always intersect the isothermal lines ($PV = \text{constant}$). Adiabatic lines are

steeper than isothermal lines.

For the adiabatic expansion from B to C, the work is equal to the change in internal energy, which is proportional to ΔT .

$$(22.11) \quad \Delta U_{BC} = \frac{3}{2}nR(T_C - T_h) = \cancel{Q_{BC}} + W_{BC} < 0$$

$$\Delta U_{DA} = \frac{3}{2}nR(T_h - T_c) = \cancel{Q_{DA}} + W_{DA} > 0$$

The equal and opposite amount of work is done on the branch with adiabatic contraction from D to A, between the same initial and final temperatures. The total work on the adiabatic lines is therefore 0. We need only to consider the work done along the isothermal branches. This is consistent with our definition (22.2) for the work in a cyclical process in which the gas does work.

$$\Delta U = 0 = |Q_h| - |Q_c| - W_{eng};$$

A to B: Isothermal expansion, $\Delta U=0$ because $\Delta T=0$; heat Q_h enters the system ($Q_h > 0$). The gas expands, raises the piston, and thus, does work. We can calculate Q_h because it is equal to the work done during that process W .

We need to make sure that both Q_h and Q_c are positive quantities.

$$(22.12) \quad \Delta U_{AB} = 0 = |Q_h| - W_{AB}$$

$$|Q_h| = |W_{AB}(T_2)| = \left| -1 \int_A^B P dV \right| = \int_A^B \frac{nRT_2}{V} dV = nRT_2 \ln \frac{V_B}{V_A} > 0$$

C to D: At this lower isothermal branch heat Q_c leaves the system ($Q_c < 0$) at the lower temperature T_1 . The gas is being compressed, work is done on it.

$$\Delta U_{CD} = 0 = |Q_c| - W_{CD}$$

$$(22.13) \quad |Q_c| = W(T_1) = \int_C^D P dV = \int_C^D \frac{nRT_1}{V} = nRT_1 \ln \frac{V_D}{V_C} < 0$$

$$|Q_c| = nRT_1 \ln \frac{V_C}{V_D} > 0$$

$$(22.14) \quad e = 1 - \frac{|Q_c|}{|Q_h|} = 1 - \frac{nRT_1 \ln \frac{V_C}{V_D}}{nRT_2 \ln \frac{V_B}{V_A}}$$

We need to get rid of the ln expressions. We have formulas to relate the volume endpoints to the higher and lower temperatures because of the adiabatic formulas:

For the adiabatic expansion between B to C, from temperatures T_2 to T_1 (T_h to T_c) we get

$$(22.15) \quad T_2 V_B^{\gamma-1} = T_1 V_C^{\gamma-1}$$

For the adiabatic expansion between A and D, from temperatures T_2 to T_1 we get:

$$(22.16) \quad T_2 V_A^{\gamma-1} = T_1 V_D^{\gamma-1}$$

Dividing equation (22.15) by (22.16) we get:

$$(22.17) \frac{T_2 V_B^{\gamma-1}}{T_2 V_A^{\gamma-1}} = \frac{T_1 V_C^{\gamma-1}}{T_1 V_D^{\gamma-1}}$$

$$(22.18) \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

This means for the efficiency:

$$(22.19) e = 1 - \frac{|Q_c|}{|Q_h|} = 1 - \frac{nRT_1 \ln \frac{V_C}{V_D}}{nRT_2 \ln \frac{V_B}{V_A}} = 1 - \frac{T_1}{T_2}$$

This is a quantitative statement of the second law of thermodynamics. It is the highest efficiency of a heat engine because it is calculated for a reversible (quasi static) process.

(22.20)

The highest possible efficiency in a heat engine is the Carnot efficiency

$$e = 1 - \frac{T_1}{T_2}$$

22.4a Problem: A Carnot engine runs between a high temperature of 500°C and a low temperature of 50°C. The isothermal expansion (upper branch) occurs between a volume of 0.500 liters and 1.00 liters. The isothermal contraction (lower branch) occurs between 2.00 l and 1.00 l. There are 2 mols of a gas involved. Calculate the **work done by the engine**, the **heat taken in Q_h** , and the **heat ejected Q_c** . Calculate the efficiency of the cycle.

Draw a PV diagram and show the area corresponding to the total work being done. Show the beginning and end points of the isothermal and adiabatic curves. Show during which branch of the cycle heat enters and leaves the engine. (Note that we defined work W as the work done on the system. In your calculations here you will find negative work for the path from A to B to C to D. The negative of this value is the work done by the engine.)

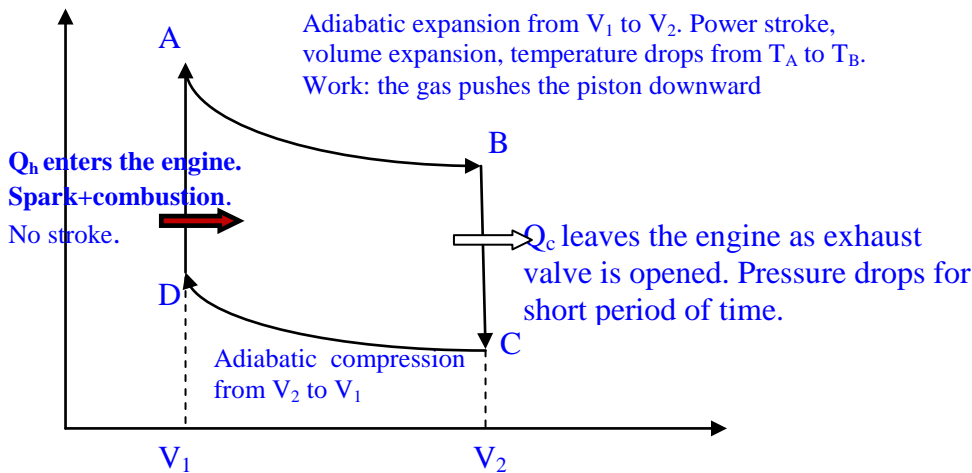
$$W = 5.19kJ, Q_h = 8.91kJ; Q_c = 3.72kJ; e = 0.582$$

$$\Delta U = 0 \Rightarrow Q = Q_h - Q_c = -W$$

$$Q_h = nRT \ln 2 = 2 \cdot 8.314 \cdot 773 \cdot 0.693 = 8.91kJ$$

$$W = Q_h \cdot e = 5.19kJ$$

22.4b In a gasoline engine (Otto engine) the compressed air-gasoline mixture is ignited through spark plugs. In a **Diesel engine** the mixture gets compressed to such a pressure that the gasoline-air mixture ignites by itself. In both cases the pistons cycle between the same compressed and decompressed volumes of air. In comparison to the Carnot cycle that means that the volumes V_B and V_C are the same, V_2 ; so are the volumes V_A and V_D , V_1 . Also, The adiabatic processes occur between A and B, as well as C and D. (There are 4 different temperatures at the intersecting points. The isotherms are located below the adiabatic curves.)



$$(22.21) \quad e = 1 - \left| \frac{Q_c}{Q_h} \right|; W_{eng} = |Q_h| - |Q_c|$$

We can calculate Q by noting that on the respective branches vertical $W=0$ and therefore

$$(22.22) \quad \Delta U_{BC} = Q_c = nC_V (T_B - T_C) > 0$$

And

$$(22.23) \quad \Delta U_{DA} = Q_h = nC_V (T_A - T_D) > 0$$

Note that we have four different temperatures at the intersection points.

Furthermore we know that on the adiabatic branches we have:

$$(22.24) \quad T_A V_1^{\gamma-1} = T_B V_2^{\gamma-1}$$

And

$$(22.25) \quad T_D V_1^{\gamma-1} = T_C V_2^{\gamma-1}$$

$$(22.26) \quad (T_A - T_D) V_1^{\gamma-1} = (T_B - T_C) V_2^{\gamma-1} \Rightarrow \frac{(T_B - T_C)}{(T_A - T_D)} = \frac{V_1^{\gamma-1}}{V_2^{\gamma-1}} = \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

$$(22.27) \quad e = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_B - T_C}{T_A - T_D} = 1 - \left(\frac{V_1}{V_2} \right)^{\gamma-1} = 1 - \frac{1}{\left(\frac{V_2}{V_1} \right)^{\gamma-1}}$$

Therefore we get the efficiency of an Otto engine in terms of the compression ratio, the ratio between the higher volume and the lower volume: $\frac{V_2}{V_1} > 1$.

Note that the smaller volume is V_1 and the larger volume is V_2 . We express the efficiency of such an engine directly by the compression ratio:

$$(22.28) \quad e = 1 - \left(\frac{V_1}{V_2} \right)^{\gamma-1} = 1 - \frac{1}{\left(\frac{V_2}{V_1} \right)^{\gamma-1}} = 1 - \frac{T_B}{T_A} = 1 - \frac{T_C}{T_D}$$

This compression ratio is much higher in a Diesel engine than in an Otto engine.

Example: The pressure in a Diesel engine varies from 1 to 20 atmospheres during the adiabatic compression. Find the efficiency of the engine. To get the compression ratio we use the adiabatic equations between the vertical branches:

$$(22.29) \quad P_A V_1^\gamma = P_B V_2^\gamma \Rightarrow \frac{P_A}{P_B} = \frac{V_2^\gamma}{V_1^\gamma} \Rightarrow \frac{V_2}{V_1} = \left(\frac{P_A}{P_B} \right)^{\frac{1}{\gamma}} = \left(\frac{20}{1} \right)^{\frac{1}{1.4}} = 8.50$$

The compression ratio is 8.5, therefore we get the efficiency from (22.28)

$$(22.30) \quad e = 1 - \frac{1}{\left(\frac{V_2}{V_1} \right)^{\gamma-1}} = 1 - \frac{1}{8.5^{0.4}} = 57.5\%$$

22.5 Entropy.

As we mentioned before, systems left to themselves (isolated systems) tend to evolve in a direction of greater disorder. Entropy S , is a measure of this disorder. All macroscopic processes occur in such ways that the **total net entropy of all systems interacting with each other increases**. This process goes hand in hand with the notion that natural processes evolve in the direction of lowest possible energy.

The **increase in disorder of one system always outweighs the increase in order of another system**. For example, the organisation of molecules into one particular pattern of a plant, comes at the cost of order in its environment. **Entropy in the macroscopic universe is simple minded, it only increases, somehow like time**. All of these macroscopic processes are irreversible. The disorganisation can be described in terms of the change in entropy from one state to the other:

$\Delta S = k_b \ln(\text{number of all possible microstates})$ The entropy can be looked at as an energy that cannot be retrieved without creating larger energy losses somewhere else. Thus, the impossibility to do work at a 100% efficiency is related to the unavoidable increase in entropy.

22.5b Macrostates and Microstates.

Consider again the free expansion of a gas from a compartment of volume A to the compartment of volume B, both of which are equal in size. If we have four molecules to start with in one container, after a while we will most likely have 2 molecules in each compartment. In the example of a free adiabatic expansion we considered just two of five possible macro states. We have an initial and a final state with 0 particles being in one compartment and four in the other. These are the states with lowest probability. The probability of finding two molecules in each container is the highest probability of any of these so-called macro-states. It does not matter which of the four molecules is in either compartment. All that matters for the definition of the macro-state is the number of molecules.

We can see that there are the following 5 macrostates possible.

Here are the macro-states:

- 0 in A and 4 in B
- 1 in A and 3 in B
- 2 in A and 2 in B
- 3 in A and 1 in B
- 4 in A and 0 in B

In **macro-states** the overall fact of **a certain number of molecules in a particular state counts**, not the composition in terms of individual particles. Such overall situations correspond to the **macroscopic quantities like pressure, temperature, and volume, and total number of particles**. (All that matters is how many particles are in a state, not which particular ones of the indistinguishable particles.)

The **most likely** situation (macro-state) corresponds to that with an equal number of molecules in each compartment, 2 in A and 2 in B. If we have four molecules to begin with, we figure out in how many different ways (micro-states) this macro-state can be achieved. Each such path, possibility, where we now label each molecule, counts as a micro state.

If we distinguish the individual molecules by labeling them each with a number 1 through 4 there are $2^4 = 16$ different configurations (micro-states) available. There are 16 different ways in which the macrostate “2 molecules in each compartment” can be achieved.

Each one of the particles can be in one of 2 different containers (A or B) at a time. We can see that the most probable macrostate is the one with equal numbers of molecules in each volume. We can see from the next figure that the largest number of micro-states corresponds to this macro-state. There are many more possible paths (microstates) available to achieve this most probable macro-state.

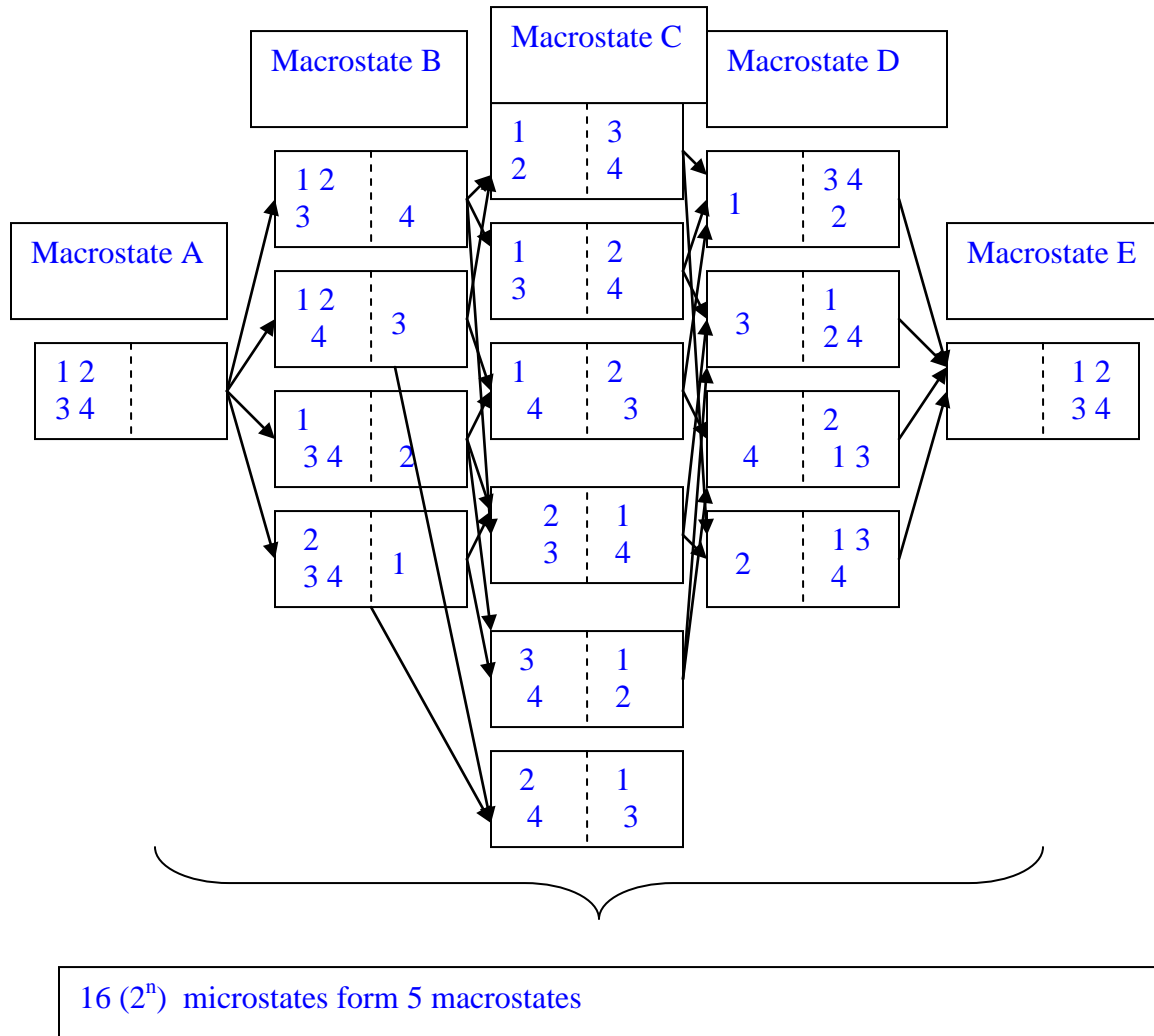
Entropy change between two states is defined as:

$$(22.31) \quad \Delta S = k_B \ln(\text{number of micro-states})$$

We define the concept of microstates as the number of paths in which a particular configuration of a state can be obtained. In our following example the two different initial and final states are

- a) the state in which four particles are contained in one side of the container and

- b) the state in which we have an equal number of particles in both containers.
 The law of entropy states that any natural process evolves towards the state of highest probability, which is the state in which we have an equal number of particles in each state. In our case this is the macrostate C.
 We simply count in how many different ways state b) (any macrostate C) can be reached from state a) (Macrostate A or E), given that all particles are identical. This is a purely statistical count.



We are distributing N particles into two possible chambers. There are 2^N ways (microstates, micro-paths) to do that. It is therefore 2^N times more probable to have the 4 molecules distributed equally (2 in each) in both containers (macro-state) than having all molecules in one container. The entropy of this state is higher by

$$(22.32) \quad \Delta S = k_B \ln 2^N = k_B N \ln 2$$

than the state in which all molecules are in one single box.

In general, this becomes:

$$(22.33) \quad \Delta S = k_B \ln(\text{number of micro-states})$$

To distribute n moles of a gas in two chambers we have 2^{nN_A} microstates. The entropy change is therefore:

$$(22.34) \quad \Delta S = k_B \ln(2^{nN_A}) = nN_A k_B \ln 2 = nR \ln 2$$

This is the entropy change for a free, adiabatic expansion of n moles of an ideal gas into 2 equally sized compartments.

This law can also be expressed in terms of the probability to encounter a particular macrostate. In our example we have 16 equivalent microstates which correspond to the 5 macro-states of having 2 particles in each chamber. **To encounter any particular one of these 16 microstates in one single observation** has a probability of $2^{-4}=1/16=1/P$. If we have 10 particles to distribute we have $2^{10}=1024 \approx 10^3$ microstates. For a hundred particles we have $2^{100}=1024^{10} \approx 10^{30}$. The probability to find a single particular state occupied in the case of N particles is equal to 2^{-N} .

The entropy is defined in terms of the probability to encounter a microstate $1/P$ through:

$$(22.35) \quad S = k_B \ln P = -k_B \ln P^{-1} = -k_B \ln(\text{probability to find a particular macrostate occupied})$$

$$[S] = \frac{J}{K}$$

P is the probability to form a macrostate through the many microstates. The inverse: $1/P$ is the probability to find such a state occupied.

All we need to remember in this context is that the fact that events evolve in the direction of greater probability is the same as saying that the entropy increases.

22.6 Macroscopic Entropy Definition.

For our purposes another definition of entropy is more relevant: The entropy change in a reversible process is given by:

$$(22.36) \quad dS = \frac{dQ_{reversible}}{T}$$

As natural processes are irreversible, the actual entropy change is larger than the one given by equation(22.36). We can calculate a lower limit for the entropy change by substituting irreversible processes in nature by reversible processes for which we can define the thermodynamic state variables at every point of the path through quasistatic thought-processes.

$$(22.37) \quad dS \geq \frac{dQ_{reversible}}{T}; \Delta S_{AB} \geq \int_A^B \frac{dQ_{reversible}}{T}$$

The entropy $S(P,V,T)$ is, like the internal energy U , only dependent on the initial and final state of a thermodynamic process, which again means that the entropy change for a complete cycle is equal to 0.

Furthermore we can calculate the entropy change for an irreversible process by calculating the change of entropy for a reversible process as long as the initial and final states of the irreversible and reversible processes are the same.

Let us calculate the change of entropy for a gas expanding freely, and adiabatically into a vacuum, doubling its original volume. As we have seen earlier, this is an irreversible process with:

$$(22.38) \quad Q = 0; \Delta T = 0; W = 0; \Delta U = 0$$

We need to find a series of reversible (quasi-static) processes with the same initial and final states as in the free adiabatic expansion. The volume doubles, the temperature remains the same. We can achieve the same expansion of a gas by allowing it to do work against a piston (during which work is done **by** the system, or negative work is done **on** the system) in an **isothermal** quasistatic, reversible process. As entropy change is path-independent, only the initial and final values matter, not the path.

$$(22.39) \quad dS = \frac{dQ_r(P,V,T)}{T}$$

For an isothermal process the change in internal energy is 0 and we have

$$(22.40) \quad dQ_r = -dW = PdV = \frac{nRT}{V}dV \quad \text{from } P = \frac{nRT}{V}$$

$$(22.41) \quad \Delta S = S_f - S_i = \int_i^f \frac{dQ_r}{T} = \int_i^f \frac{nRT}{T} \frac{dV}{V} = nR \ln \frac{V_f}{V_i} = nR \ln 2$$

The actual entropy change would be greater than this minimal value for a reversible process.

Note that this result is the same as the one we got through our microscopic approach in (22.34).

22.7 Entropy Change for a Quasi Static Reversible Process of an Ideal Gas.

Recall that quasi-static means that the system is in thermodynamic equilibrium at all times during the process. Any state change of an ideal gas involves the three state variables P , V , T . Let us here calculate the entropy change of a gas that expands from an initial volume V_i to a final volume V_f while undergoing a temperature change from T_i to T_f .

The three state variables are always connected by the ideal gas law. $PV=nRT$.

For the entropy change ΔS we need to know the heat change Q which is implicitly defined by the first law of thermodynamics $\Delta U=Q+W$. **For a reversible process we can write this in terms of infinitesimal changes:**

$$(22.42) \quad \delta Q = dU - \delta W = dU + PdV$$

This leads to

$$(22.43) \quad \Delta S = \frac{\Delta Q}{T} = \frac{\Delta U - \Delta W}{T}$$

The **internal energy U** of an ideal gas depends only on the initial and final temperature and we have shown earlier that

$$(22.44) \quad dU = nC_v dT .$$

The change in work is always given by (No path specified):

$$(22.45) \quad W = -PdV \Rightarrow dW = -PdV = -nRT \frac{dV}{V}$$

This is not **necessarily an isothermal process**, T can change.

Now we can perform the integration, noting that in order to obtain the entropy change we must divide the change in heat by the temperature T,

$$\Delta S = \int_i^f \frac{\delta Q_r}{T}; \delta Q_r = dU - \delta W = nC_v dT + PdV$$

$$(22.46) \quad P = \frac{nRT}{V} \Rightarrow dS = \frac{\delta Q_r}{T} = nC_v \frac{dT}{T} + \frac{nR}{V} dV$$

The infinitesimal change of the entropy is a total derivative, which is why we use dS and not δS

$$(22.47) \quad \boxed{dS = \frac{\delta Q_r}{T} = nC_v \frac{dT}{T} + nR \frac{dV}{V}}$$

If we integrate this from (i) to (f) we see that we get our result without specifying a path: (In our calculation of the entropy change we do not need to specify any path, just the initial and final state variables.)

$$(22.48) \quad \boxed{\Delta S = \int_i^f \frac{dQ_r}{T} = nC_v \int_{T_i}^{T_f} \frac{dT}{T} + nR \int_{V_i}^{V_f} \frac{dV}{V} = nC_v \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}}$$

We confirm that the entropy function depends only on initial and final states, and not on the path taken.

As all macroscopic processes of heat exchange are irreversible we need to find equivalent processes which are quasi-static and/or reversible. This often boils down to replacing macroscopic temperature, pressure, or volume changes by microscopic ones, i.e. we use integration over infinitesimal (reversible) steps.

22.7a Entropy Changes During Phase Changes:

The entropy change of the melting substance in a melting process is clearly equal to the latent heat mL divided by the temperature at which the melting occurs:

$$(22.49) \quad \Delta S_{\text{melting}} = \frac{mL}{T_{\text{melting}}}$$

The heat necessary comes from the environment which is at a higher temperature, the net entropy change is positive.

22.7b The entropy change during a thermal conduction is equal to the heat loss at T_h minus the heat-gain at the lower temperature T_c . As the amount of heat Q lost at the higher temperature T_h is equal to the amount of heat gained at the lower temperature, and as the temperature appears in the denominator, the entropy change is always positive:

$$(22.50) \Delta S = \frac{-Q_h}{T_h} + \frac{Q_c}{T_c} = Q \left(\frac{1}{T_c} - \frac{1}{T_h} \right) > 0$$

Problem: Calculate the entropy change occurring during the heat flow through a steel bar of length 10cm and cross section 2.0cm^2 , one end of which is at a temperature of the steam point of water, the other at the freezing point of water:

$k_{\text{steel}} = 79.5\text{W/mK}$.

$$(22.51) \quad \dot{Q} = \frac{kA}{L} |\Delta T| = \frac{79.5 \cdot 2 \cdot 10^{-4}}{0.1} 100\text{W} = 0.16\text{W}$$

The entropy transfer per second is therefore:

$$(22.52) \quad 0.16\text{W} \left(\frac{1}{273\text{K}} - \frac{1}{373\text{K}} \right) = 1.57 \cdot 10^{-4} \frac{\text{W}}{\text{K}}$$

22.7c Entropy Change in Calorimetric Processes:

When two different substances at different temperatures are in close contact with each other, heat will flow from the hotter substance to the cooler substance until a final equilibrium temperature is reached. This is clearly an irreversible process. However, we can find an equivalent process in which for example the cooler substance is put into contact with a heat reservoir at an infinitesimally higher temperature. A small amount of heat will flow from the heat-reservoir to the cooler substance in an approximately reversible process. This will be repeated until the cooler substance has reached the final temperature. The same process is used to cool down the hotter substance by putting it in contact with successive heat-reservoirs of infinitesimally decreasing temperatures.

First substance at lower temperature: $m_1; c_1; T_1$

(22.53) Second substance at higher temperature: $m_2; c_2; T_2$

Final, equilibrium temperature: T_f

$$\underbrace{m_1 c_1 (T_f - T_1)}_{\text{heat gained } Q_1 > 0} = \underbrace{m_2 c_2 (T_2 - T_f)}_{\text{heat lost } Q_2 < 0}$$

$$(22.54) \quad m_1 c_1 T_f - m_1 c_1 T_1 = m_2 c_2 T_2 - m_2 c_2 T_f$$

$$m_1 c_1 T_f + m_2 c_2 T_f = m_2 c_2 T_2 + m_1 c_1 T_1$$

$$(22.55) \quad T_f = \frac{m_2 c_2 T_2 + m_1 c_1 T_1}{m_1 c_1 + m_2 c_2}$$

Now we use the integral form of the entropy formula to calculate the entropy change for both substances: The first substance gains heat at the lower temperature T_1 , therefore $Q_1 > 0$ is positive. The second substance gives up heat at the higher temperature T_2 , therefore $Q_2 < 0$ is negative.

$$(22.56) \Delta S = \int_{T_1}^{T_f} \frac{dQ_1}{T} + \int_{T_2}^{T_f} \frac{dQ_2}{T} = \int_{T_1}^{T_f} \frac{m_1 c_1}{T} dT + \int_{T_2}^{T_f} \frac{m_2 c_2}{T} dT = \int_{T_1}^{T_f} \frac{m_1 c_1}{T} dT - \int_{T_f}^{T_2} \frac{m_2 c_2}{T} dT$$

$$(22.57) \Delta S = m_1 c_1 \ln \frac{T_f}{T_1} - m_2 c_2 \ln \frac{T_2}{T_f}$$

The entropy is obviously always positive in such heat exchanges.

Example: 50 g of aluminum ($c=0.215 \text{ cal/gC}^\circ$) at 100°C are immersed into 100g of water at 20°C . Find the entropy change for the combination of aluminum plus water. We need to equate the heat loss of aluminum with the heat gain of water:

$$(22.58) m_{Al} c_{Al} (100 - T_f) = m_w c_w (T_f - 20)$$

$$T_f = 27.8^\circ$$

$$(22.59) dQ = mcdT$$

The entropy change for aluminum and requires an integration:

$$(22.60) \Delta S_{Al} = \int_i^f \frac{dQ_f}{T} = \int_{373}^{300.8} \frac{m_{Al} c_{Al}}{T} dT = m_{Al} c_{Al} \ln \frac{300.8}{373} = -50 \cdot 0.215 \cdot 0.215 \frac{\text{cal}}{\text{C}^\circ} = -2.31 \frac{\text{cal}}{\text{C}^\circ}$$

The same for water:

$$(22.61) \Delta S_w = m_w c_w \int_{293}^{300.8} \frac{dT}{T} = 100 \ln \frac{300.8}{293} = 2.63 \frac{\text{cal}}{\text{C}^\circ}$$

The total entropy change is 0.313 cal/K .

Problem: 100g of ice at 0°C are immersed into 200g of water at 60°C . Calculate the entropy change of the mixture after thermodynamic equilibrium has been established.

$$Q_{ice} = mL = 100 \cdot 80 \text{ cal} = 8000 \text{ cal}$$

$$m_w \cdot c_w \cdot \Delta T = 200 \text{ g} \cdot 1 \frac{\text{cal}}{\text{gC}^\circ} \Delta T = 8000 \text{ cal} \Rightarrow \Delta T = 40 \text{ C}^\circ$$

This heat is extracted from the hot water:

$$T_{w,f}^1 = 20^\circ\text{C}$$

The temperature of the water drops from 60 to 40°C due to the melting of the ice.

Now we need to calculate the final temperature of the water mixture:

$$100(T_f - 0) = 200(20 - T_f)$$

$$T_f = 13.3^\circ\text{C}$$

We could also have calculated this right from the beginning:

$$\begin{aligned}
 m_{ice}L + m_{icewater}c_w(T_f - 0) &= mc_w(60 - T_f) \\
 (22.62) \quad 100 \cdot 80cal + 100g \cdot \frac{1cal}{gC^\circ}T_f &= 200g \cdot \frac{1cal}{gC^\circ}60C^\circ - 200g \cdot \frac{1cal}{gC^\circ}T_f \\
 T_f &= 13.3^\circ C
 \end{aligned}$$

For the entropy change we get:

$$\begin{aligned}
 \Delta S &= \frac{Q_{ice}}{T} + m_1c_1 \int_{273}^{286.3} \frac{dT}{T} + m_2c_2 \int_{333}^{286.3} \frac{dT}{T} = \\
 (22.63) \quad &= \frac{8000cal}{273K} + 100g \frac{1.00cal}{gK} \ln \frac{286.3}{273} + 200g \frac{1.00cal}{gK} \ln \frac{286.3}{333} = \\
 &= (29.3 + 4.76 - 30.2) \frac{cal}{K} = 3.84 \frac{cal}{K}
 \end{aligned}$$

Optional:

22.8 Thermodynamic Equilibrium:

A system of physical process is said to be in equilibrium if it does not change in time. The equilibrium is stable if a change from its equilibrium position causes the system to revert to its previous equilibrium point. It is unstable if any such change causes the system to move further away from its equilibrium point. It is indifferent if a change does not influence the equilibrium in either way.

In mechanics, the equilibrium points are given by the extreme points of the potential energy. A minimum of the potential energy curve corresponds to a stable equilibrium point.

The function in thermodynamics which corresponds to the potential energy in mechanics is the entropy S , provided that we deal with an isolated system, which does not exchange energy or mass with the environment. In this situation, **a system is in equilibrium if it is at the point of maximum entropy**. Any change away from this point will entail processes which tend to increase the entropy to the maximum.

In a system that can exchange energy with the environment, but not mass, we need to also consider the entropy change of the environment. We have done this to some extent in a few of the previous problems. In the last example (22.63) we could consider ice as the system and the water as the environment. Such processes evolve by themselves only if

$$(22.64) \quad \Delta S_{system} + \Delta S_{env} \geq 0$$

We saw that we needed to calculate the sum of entropy changes of the environment and the system.

We are at the equilibrium point if

$$(22.65) \quad \Delta S_{system} + \Delta S_{env} = 0$$

This point was reached in the previous example when the water is at a temperature of $13.3^\circ C$, where we treated ice and water as one system. As long as the temperature is above or below that temperature the system+environment keeps changing until it has reached the thermodynamic equilibrium.

If, in addition to heat exchange ΔQ , work ΔW is involved in the process, we can write for the system plus environment:

$$(22.66) \quad \Delta S = \frac{\Delta Q}{T} = \frac{\Delta U - \Delta W}{T} \text{ or } \Delta U - \Delta W - T\Delta S = 0$$

If work can only be done by pressure on a piston, we have $\Delta W = -P\Delta V$, and we get:

$$(22.67) \quad \boxed{\Delta U + P\Delta V - T\Delta S = 0}$$

If we keep the volume constant, like in a chemical process inside a closed flask, we get:

$$(22.68) \quad \Delta U - T\Delta S = 0$$

If, in addition, we maintain a constant temperature, equation (22.67) becomes:

$$(22.69) \quad \Delta \left(\underbrace{U - TS}_{\substack{\text{Free energy } F \\ \text{or Helmholtz potential}}} \right) = 0; V \text{ and } T \text{ are constant}$$

Free Energy F (Helmholtz potential):

$$(22.70) \quad \boxed{\begin{array}{l} \text{Under isothermal and iso - volumetric conditions} \\ \text{the thermodynamic equilibrium is given by the minimum Free Energy } F: \\ F = U - TS; \Delta F = 0 \text{ with } T \text{ and } V \text{ constant.} \end{array}}$$

Note that the term “free” is used when the product TS is subtracted.

For constant pressure and constant temperature, equation (22.67) is equivalent to

$$(22.71) \quad \Delta \left(\underbrace{U + PV - TS}_{\substack{\text{Free Enthalpie or Gibbs potential}}} \right) = 0 \text{ temperature and pressure are constant}$$

Free Enthalpie G (Gibbs potential):

$$(22.72) \quad \boxed{\begin{array}{l} \text{Under isothermal and isobaric conditions (T, P constant)} \\ \text{we obtain thermodynamic equilibrium if the free Enthalpie } G \text{ is at a minimum, } \Delta G = 0: \\ G = U + PV - TS \end{array}}$$

This means for example, that a chemical reaction, with T and P, constant will spontaneously occur if its free enthalpie will decrease in the process. Processes like these occur in organisms all the time.

In some processes heat exchange is not possible, but work is. This means that $T\Delta S = \Delta Q = 0$ in (22.72). We get the function called **Enthalpie H**: $\Delta(U + PV) = 0$.

Under adiabatic-isobaric conditions ($T\Delta S = 0$, P constant)

we obtain thermodynamic equilibrium if the Enthalpie H is at a minimum, $\Delta H = 0$:

$$(22.73) \quad H = U + PV$$

If volume is maintained constant, we see that enthalpie and internal energy are the same.

We achieve equilibrium if $\Delta U = 0$, the internal energy is at a minimum.

In chemical reactions in which the number of moles of the products are variables, we need to include those in our formulas. This is left to chemistry.

Optional: 22.9 Calculating the critical temperature of a real gas:

An interesting application of the enthalpie function occurs in the understanding of gas liquification. An ideal gas would never liquify! A real gas however can be liquified. In a free expansion of a real gas the temperature does change. Its equation of state is given by the van der Waals equation mentioned in chapter 19.:

$$\left(P + \frac{a}{V_{mol}^2}\right)(V_{mol} - b) = RT, \left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

$\frac{a}{V_{mol}^2}$ is an internal pressure deriving from the attractive force of

the molecules to each-other: $F = PA$ (pressure times area). The potential energy U_{attr} involved in this attraction can be guessed at by:

$$(22.74) \quad U_{attr} = -Fx = -PAx = -PV = \frac{-a}{V}$$

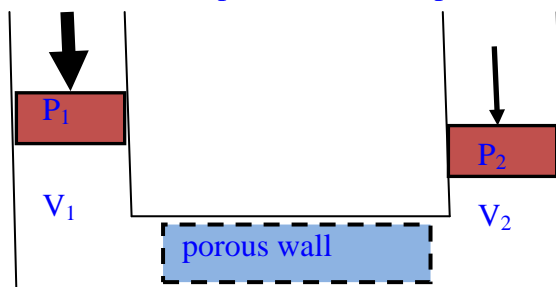
b is the volume occupied by at single finite mole of particles.

The van der Waals equation can also be written as:

(22.75)

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

Let us study this in an experiment illustrating the Joule-Thomson effect: The gas in the left chamber is under the constant pressure P_1 and gets slowly pushed into the volume to the right which is under the constant pressure P_2 . The porous wall prevents any turbulence. The whole



volume of gas to the left gets pressed into the right chamber. We assume that the pressure in the chamber to the right is smaller than the pressure in the chamber to the left.

The net work done on the gas is therefore: $P_1V_1 - P_2V_2$ which is an

increase in the internal energy of the gas. In real experiments we observe an increase in the

temperature for CO₂ and air, and a decrease for H₂.

In order to conveniently describe the process we use the enthalpie function which contains the additional PV term, $H = U + PV$. The enthalpie remains constant because

$$(22.76) \quad \begin{aligned} P_1V_1 - P_2V_2 &= U_2 - U_1 \Rightarrow \\ \underbrace{P_1V_1 + U_1}_{H_1} &= \underbrace{P_2V_2 + U_2}_{H_2} \end{aligned}$$

Let us calculate the enthalpie for a van der Waals gas. The internal energy for one mole of such a gas depends on the number of degrees of freedom f :

$$(22.77) \quad U = \frac{f}{2}RT$$

The internal pressure results in a negative work term (work is positive if it is exerted on the system!) $-\frac{a}{V^2}V = -\frac{a}{V}$ which must be added to the internal energy. The additional PV term in the

enthalpie also contains the $-\frac{a}{V^2}$. Again, we must use the negative term because it corresponds to inside pressure. Thus we get the total enthalpie function

$$(22.78) \quad \begin{aligned} H &= \underbrace{\frac{f}{2}RT - \frac{a}{V}}_{\text{modified internal energy } U} + \underbrace{\left(\frac{RT}{V-b} - \frac{a}{V^2}\right)V}_P; \text{ with } P = \frac{RT}{V-b} - \frac{a}{V^2} \\ H &= \frac{f}{2}RT - \frac{a}{V} + \left(\frac{RT}{V-b} - \frac{a}{V^2}\right)V \end{aligned}$$

The enthalpie function is a total differential, which is now just a function of V and T . We simplify the function factoring out RT :

$$(22.79) \quad H = RT \left(\frac{f}{2} + \frac{V}{V-b} \right) - \frac{2a}{V}$$

The total change in this function must be 0, if H is constant.

$$(22.80) \quad dH = \frac{\partial H}{\partial T}dT + \frac{\partial H}{\partial V}dV = 0$$

$$(22.81) \quad \begin{aligned} H &= RT \left(\frac{f}{2} + \frac{V}{V-b} \right) - \frac{2a}{V} \\ \frac{\partial H}{\partial T} &= R \left(\frac{f}{2} + \frac{V}{V-b} \right); \\ \frac{\partial H}{\partial V} &= RT \left(\frac{1}{V-b} - 1 \frac{V}{(V-b)^2} \right) + \frac{2a}{V^2} = RT \left(\frac{V-b-V}{(V-b)^2} \right) + \frac{2a}{V^2} = \frac{-RTb}{(V-b)^2} + \frac{2a}{V^2} \end{aligned}$$

From (22.80) we solve for dT :

$$(22.82) \quad dT = -\frac{\frac{\partial H}{\partial V}}{\frac{\partial H}{\partial T}}dV = -dV \frac{\frac{-RTb}{(V-b)^2} + \frac{2a}{V^2}}{R \left(\frac{f}{2} + \frac{V}{V-b} \right)} = \frac{\frac{Tb}{(V-b)^2} - \frac{2a}{RV^2}}{\frac{f}{2} + \frac{V}{V-b}}dV$$

We approximate $V-b$ by V to get:

$$(22.83) \quad dT \approx \frac{\frac{Tb}{V^2} - \frac{2a}{RV^2}}{\frac{f}{2} + \frac{V}{V}} dV = \frac{1}{RV^2} (TbR - 2a) = \frac{TbR - 2a}{RV^2 \left(\frac{f}{2} + 1 \right)} dV$$

During an expansion of the gas, dV is positive; the denominator is always positive. The numerator can be positive or negative according to the value for T . The equation

$$(22.84) \quad TbR - 2a = 0$$

defines the inversion temperature T_i :

$$(22.85) \quad T_i = \frac{2a}{Rb}$$

The critical temperature T_c of a real gas is the temperature above which the gas cannot be liquified, no matter how large the pressure. That critical temperature is:

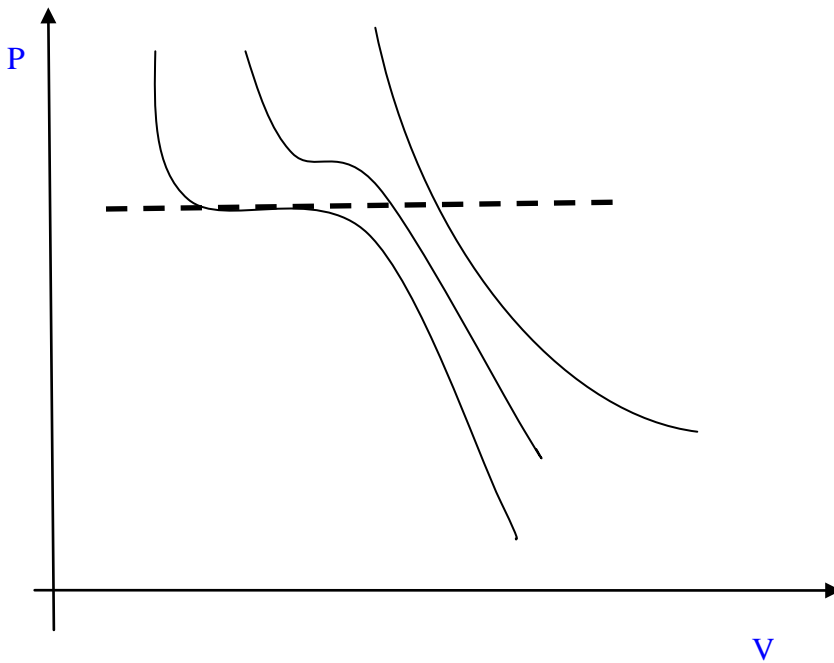
$$(22.86) \quad \begin{aligned} CO_2 &: 304.2K \\ O_2 &: 154.4K \\ N_2 &: 126.1K \\ H_2 &: 33.3K \\ He &: 5.3K \end{aligned}$$

The critical temperature for a real gas is given by:

$$(22.87) \quad T_c = \frac{8a}{27Rb}$$

It corresponds to the inflection point in the isotherm of a PV diagram for a real gas. Below are three isotherms with increasing temperatures for the isotherms from left to

right.



$$(22.88) \quad \left(\frac{\partial P}{\partial V} \right)_{T=\text{constant}} = 0 = \left(\frac{\partial^2 P}{\partial V^2} \right)_{T=\text{constant}}$$

$$(22.89) \quad \boxed{\begin{aligned} P &= \frac{RT}{V-b} - \frac{a}{V^2} \\ \frac{\partial P}{(\partial V)_T} &= \frac{-RT}{(V-b)^2} + \frac{2a}{V^3} = 0 \\ \frac{\partial^2 P}{(\partial V^2)_T} &= \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} = 0 \end{aligned}}$$

We obtain the critical temperature by dividing the last two equations into each other:

$$(22.90) \quad \begin{aligned} \alpha) \quad \frac{RT}{(V-b)^2} &= \frac{2a}{V^3} \Rightarrow \\ \beta) \quad \frac{2RT}{(V-b)^3} &= \frac{6a}{V^4} \Rightarrow \frac{\beta}{\alpha} \\ \frac{2}{V-b} &= \frac{3}{V} \Rightarrow V-b = \frac{2}{3}V \Rightarrow V = 3b \end{aligned}$$

Substituting $V_c=3b$ into α gives us the desired relationship:

$$V = 3b = \text{critical volume}$$

$$(22.91) \quad \frac{-RT}{(3b-b)^2} = \frac{-2a}{27b^3} \Rightarrow \frac{RT}{4b^2} = \frac{2a}{27b^3} \Rightarrow T_c = \frac{2a}{27b^3} \frac{4b^2}{R} = \frac{8a}{27Rb}$$

The inversion temperature and the critical temperature are therefore related:

$$(22.92) \quad T_i = 6.75T_c$$

Furthermore, inserting critical volume $3b$ and critical temperature into $P = \frac{RT}{V-b} - \frac{a}{V^2}$

we get the critical pressure below which no phase-change is possible:

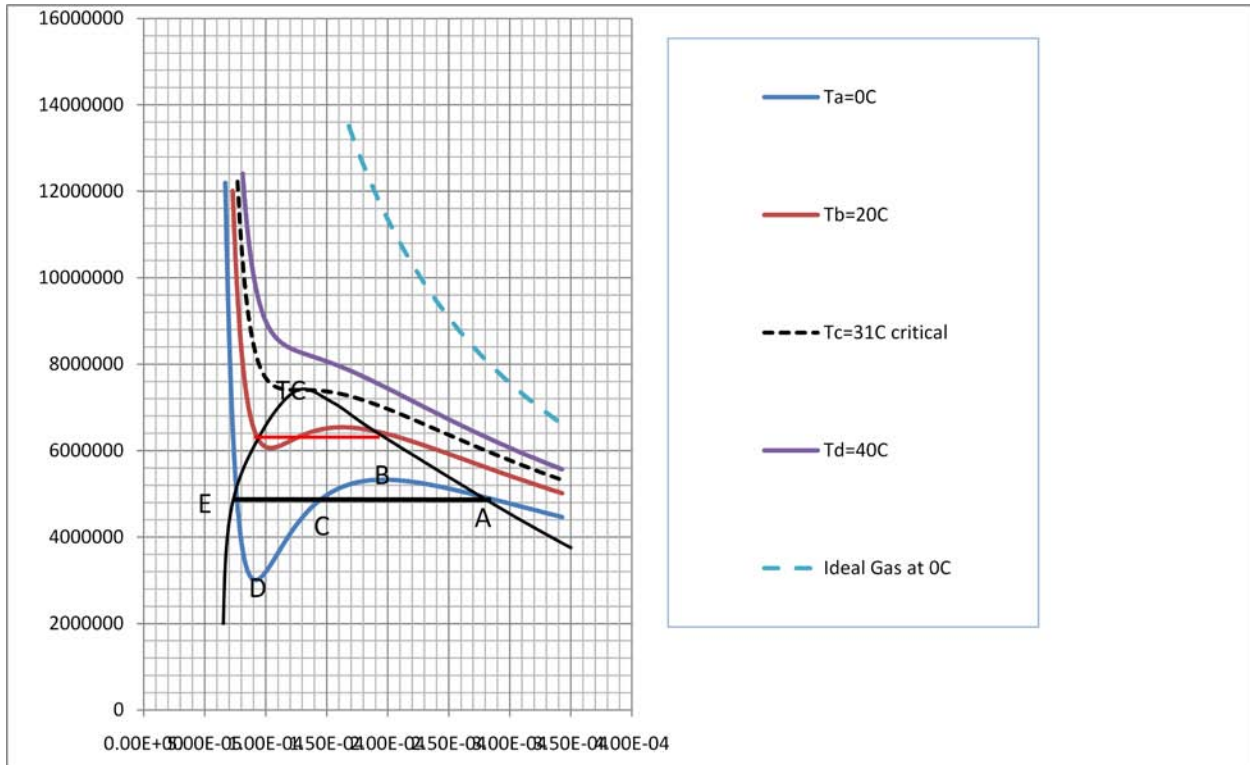
$$(22.93) \quad P_c = \frac{R \frac{8a}{27Rb}}{3b-b} - \frac{a}{9b^2} = \frac{8a}{27b \cdot 2b} - \frac{a}{9b^2} = \frac{4a-3a}{27b^2} = \frac{a}{27b^2}$$

Example: For CO₂ we measure a critical temperature of 304.2K and a critical pressure of 72.3 bar or 72.3E5 Pascals.

$$(22.94) \quad T_c = \frac{8a}{27Rb} \Rightarrow a = \frac{27Rb}{8} T_c = \frac{27 \cdot 8.314}{8} \cdot b \cdot 304.2 = 8.536 \cdot 10^3 b$$

$$(22.95) \quad P_c = \frac{a}{27b^2} \Rightarrow b^2 = \frac{a}{27P_c} = \frac{8.536 \cdot 10^3 b}{27 \cdot 72.3 \cdot 10^5} \Rightarrow b = \frac{4.4 \cdot 10^{-5} m^3}{mol}$$

$$a = 0.37 \frac{Pa \cdot m^6}{mol^2};$$



[See the file in Excel for this calculation](#)

Isothermal lines for 1 mole of carbon-dioxide.

The dashed black line corresponds to the isothermal of 31 C, above which carbon dioxide cannot be liquified, no matter how high the pressure. The Van der Waals PV graph has an inflection point at TC.

Below the solid line passing through A, TC, and E, gas and liquid coexist. When we move from right to left on the Ta=0C line we reach the point of liquification at A. The pressure increases with decreasing volume until the point B. Then the pressure decreases to the point D. It increases again beyond this point.

	R	8.314
	a	0.364
	b	4.27E-05
1cm^3	delV	1.00E-06
0C	Ta	273
20Celsius	Tb	293
31C	Tc	304
40C	Td	313