Recap… Chapter 1+2, Temperature and 0th law of TD

- How to characterise T, which scales exist?

- What is meant with thermal equilibrium?

- What is the 0th law of Thermodynamics?

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  - 0th law of Thermodynamics: If two systems are in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.

Recap… Chapter 1+2, Thermal expansion

- What is thermal expansion?

- Which property of T is important that thermometers function? Which materials are particularly well suited for measuring T?

- Give a physical explanation for the fact that thermal expansion coefficients of liquids are typically larger than that of solids.

Recap… Chapter 1+2, Thermal expansion

- What is thermal expansion?
    - The change in length of a solid, when its temperature changes is directly proportional to the T change **(valid only if T change small!!)**
    - $\Delta l = \alpha l_0 \Delta T$, α: coefficient of linear expansion
    - The change of volume of most solids, liquids and gases is proportional to the T change **(small!!)** and to the original volume $\Delta V = \beta V_0 \Delta T$, $\beta \approx 3\alpha$
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- Give a physical explanation for the fact that thermal expansion coefficients of liquids are typically larger than that of solids.
    - Solids: molecules are tightly bound in a fixed, orderly arrangement (e.g. lattice) —> when heated, the molecules vibrate more vigorously but generally maintain their relative positions, leading to a smaller overall expansion
    - Liquids: molecules are less tightly bound and can move around more freely. —> When heated, these particles move more readily, leading to a more significant increase in volume.

Recap… Thermal expansion

- Linear expansion formula $\Delta l = \alpha l_0 \Delta T$ accurately valid only for infinitely small changes in T
- For n heating steps, i.e. a continuous rise of T, the accurate formula is $l = l_0 e^{\alpha \Delta T}$

Recap… Thermal expansion

How much should I care?

“Not much, unless you melt the solid!!”

Material	Aluminium	Bras	Iron	Lead	Quartz
$\alpha\left(C^\circ\right)^{-1}$	25×10^{-6}	19×10^{-6}	12×10^{-6}	29×10^{-6}	0.4×10^{-6}

- Melting temperature of:
  Aluminium – 933 K
  Iron – 1811 K
- Estimate a 1 meter long iron bar and aluminium bar: assuming linear thermal expansion from room temperature (300 K) to melting point, the length will be:
  delta l (Al) = 25e-6/K x 633 K x 1m = 0.01583m
  delta l (Fe) = 12e-6/K x 1511K x 1m = 0.0181m
- Compare your results with that obtained from the precise formula of thermal expansion …
  l (Al) = 1m x exp(25e-6/K x 633 K) = 1.01595 —> delta l = 0.01595 m
  l (Fe) = 1m x exp(12e-6/K x 1511K) = 1.0183 —> delta l = 0.0183 m

Conceptual Questions:

- If you heat a thin circular ring in the oven, does the ring’s hole get larger or smaller? youtube demonstration: https://www.youtube.com/watch?v=nA-WJyq19H8

- Opening a tight jar lid: When the lid of a glass is tight, holding the lid under hot water for a short time will often make it easier to open. Why?

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  - It might seem counterintuitive at first, as one might expect the material to expand and close up the hole. However, it's important to remember that the expansion is uniform in all directions. Each segment of the ring, no matter where it is located, moves outward from the center of the ring as it expands, thus increasing the diameter of the hole.
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- What is meant with the anomalous behaviour of water?
- What is thermal stress and how can it be computed?

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- What is thermal stress and how can it be computed?
    - Because of thermal expansion, thermal stresses can occur if materials are rigidly fixed and T changes. The required compression to keep an object at its original length can be computed via Young’s modulus E, $\Delta l = 1/E \; P \; l_0$

Recap… Chapter 3, Gas laws

- What is the definition of an ideal gas, under which conditions can we consider a gas to be ideal?

- What are different gas laws discovered in the 17-19th centuries?

- What is the equation of state of ideal gas?

- Which corrections are assumed for real gases (van der Waals gas)?

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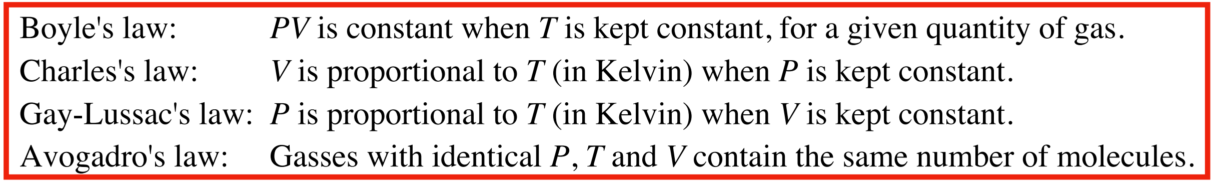

Boyle's law:	PV is constant when T is kept constant, for a given quantity of gas.
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$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

(a: pressure correction, b: volume correction)

Recap… Chapter 4, Kinetic theory of gases

- What is meant with the kinetic theory of gases, and for which type of gas is it valid?
- What is the relation between Pressure, Volume and particle velocity?
- How is the kinetic energy of ideal gas related to macroscopic T?
- How can we compute the root-mean-square velocity v_{rms} of gas particles?

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$$\boxed{v_{\text{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{2\langle K \rangle}{m}} = \sqrt{\frac{3kT}{m}}}$$

Quizzzz time

- The T of an ideal gas increases. Which of the following is true? a) the pressure must decrease. b) the pressure must increase. c) the pressure must increase while the volume decreases. d) the volume must increase while the pressure decreases. e) the pressure, the volume or both may increase.

- An ideal gas in a sealed rigid container (closed system). The average kinetic energy of the gas molecules depends mostly on a) the size of the container; b) the number of molecules in the container; c) the temperature of the gas; d) the mass of the molecules. What about the rms velocity of gas molecules?

- Why should you not put a closed, empty glass jar with the lid on tight into a campfire? What could happen?

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    - The rms velocity is additionally dependent on the mass of a particle/molecule.
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- Why should you not put a closed, empty glass jar with the lid on tight into a campfire? What could happen?
    - Heat Expansion: —> pressure increase!
    - Glass Breaking: Glass can break or shatter due to thermal stress caused by uneven heating or rapid temperature changes, in particular if the glass transitions quickly from being hot to cool.
    - —> Risk of Explosion due to combination of increased internal pressure and the thermal stress

Quizzz time

- Two ideal gases, A & B, are at the same T. If the molecular mass of the molecules in gas A is twice that of molecules in gas B, the molecules' root-mean-square velocity is a) the same in both gases; b) twice as great in A; c) 1.4 times greater in A; d) twice as great in B; or e) 1.4 times greater in B?

- In a mixture of the gases Oxygen and Helium, which statement is valid? a) The He atoms will be moving faster than the O molecules on average; b) both will be moving at the same speed. c) The O molecules will be on average moving faster. d) The kinetic energy of the He atoms will exceed that of the O molecules. e) none of the above.

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    - e) is correct. v_rms ~ 1/sqrt(m) —> This is because if the molecular mass of A is twice that of B, the rms velocity of A will be smaller by a factor of 1/sqrt(2), and hence, the rms velocity of B will be 1.4 times greater than that of A.
    - mA = 2 mB; & v_rms,B ~ 1/sqrt(mB)
    - then: v_rms,A ~ 1/sqrt(2 mB) = 1/sqrt(2) v_rms,B
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    - a) is correct, because He atoms are lighter… Oxygen (O_2) is a diatomic molecule with a molar mass of approximately 32 g/mol (16 g/mol for each oxygen atom), whereas Helium (He) is a monatomic gas with a molar mass of about 4 g/mol. Thus, oxygen molecules are heavier than helium atoms.

Recap… Chapter 5, Microstates, Macrostates of gas & thermal equilibrium

- What are Microstates and Macrostates?

- What is thermal equilibrium from a statistical point of view?

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        - Every microstate is equally probable
    - Macrostates of gas:
        - Described by global quantities, such as T, V, P, E, etc.
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- What is thermal equilibrium from a statistical point of view?
    - A system takes on that macroscopic configuration which maximises the number of microstates (highest probability)
    - The most likely macrostate is thermal equilibrium, i.e. two systems in contact have the same T ("Boltzmann argument")

$$\frac{1}{kT} = \frac{d\ln\Omega}{dE}$$

Recap… Chapter 5, Boltzmann factor and Maxwell distribution of gas speeds

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- What is probability that one gas particle has a velocity vector vx, vy, vz?

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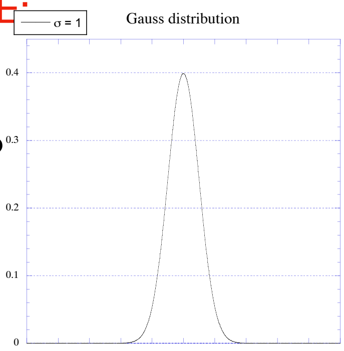
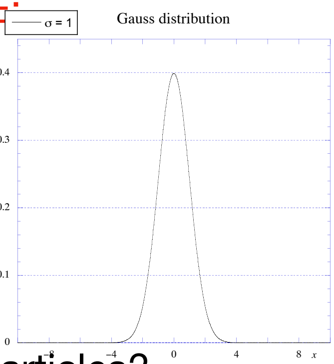


- What is the Maxwell-Boltzmann distribution of absolute speeds of gas particles?

Recap… Chapter 5, Boltzmann factor and Maxwell distribution of gas speeds

- What is the Boltzmann factor?
  - A factor to describe the probability that a system has an energy E:

$$P_r(E_r) \propto e^{-E_r/kT}$$



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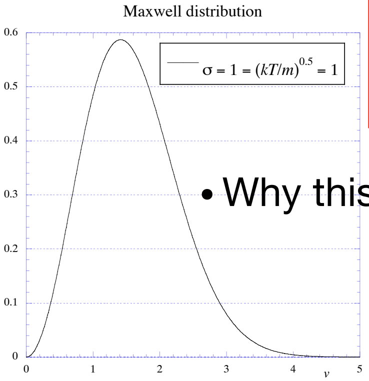
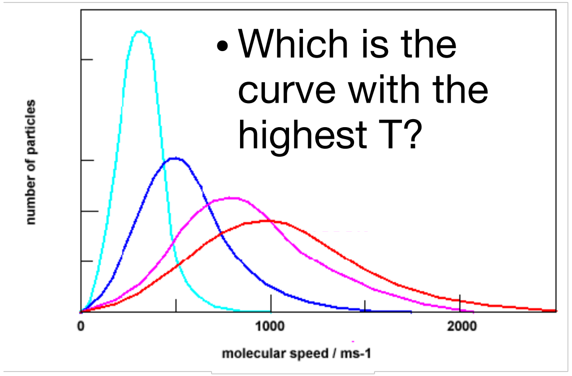


$$\boxed{F(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp\left(-\frac{m}{2kT}v^2\right)}$$

- Why this shape?



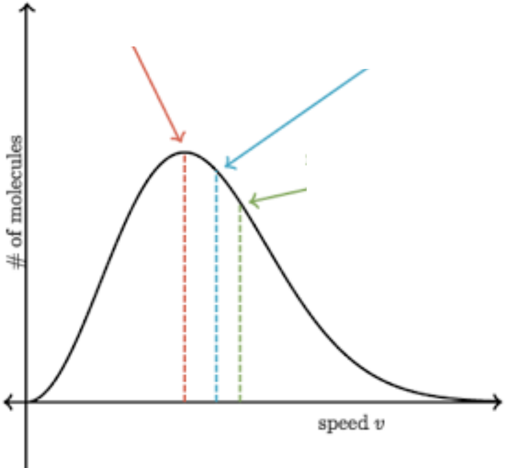
- Which is the curve with the highest T?

Recap… Chapter 5, Boltzmann factor and Maxwell distribution of gas speeds

- What are the definitions of rms, most probable and mean speed?

- Which lines in the Plot below represent the most probable speed, the average speed and the root mean square speed ?

- How do the speeds depend on T?



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- What are the definitions of rms, most probable and mean speed?

$$\boxed{\langle v\rangle = \int vF(v)dv;\ v_{rms} = \sqrt{\langle v^2\rangle};\ v_{mp} = \frac{d}{dv}F(v) = 0}$$

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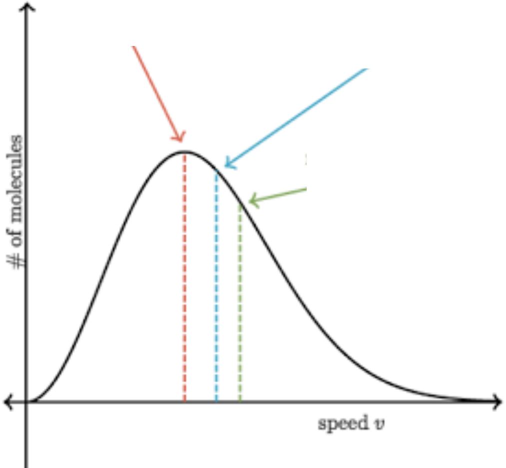

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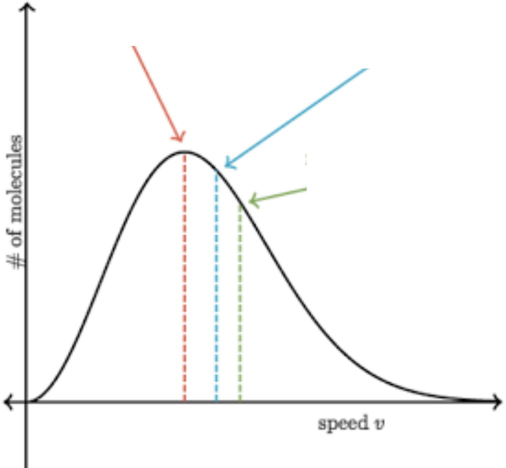
$$v_{mp} = \sqrt{\frac{2kT}{m}} <$$

$$< v_{avg} = \frac{2}{\sqrt{\pi}} v_{mp} <$$

$$< v_{rms} = \sqrt{\frac{3}{2}} v_{mp}$$



Recap… Chapter 6, Energy, heat and work in TD

- What is the internal and thermal energy? What is the internal energy of ideal gas?

- How can we describe the “flow of energy”?

- Conservation of energy: Delta $E_{int} = Q - W$ (main focus of this lecture!!)

Recap… Chapter 6, Energy, heat and work in TD

- What is the internal and thermal energy? What is the internal energy of ideal gas?
    - Internal energy E_{int}: total amount of energy of all molecules, sum of thermal and potential energy
    - Thermal energy E_{therm}: kinetic energy due to translation, rotation and vibrations
    - E_{int} of ideal gas (no potential energy) = E_{therm} $$E_{\text{int}} = E_{\text{kin}} = N\frac{m\langle v^2\rangle}{2} = \frac{3}{2}NkT = \frac{3}{2}nRT$$
    - State variables
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  - State variables
- How can we describe the “flow of energy”?
  - Heat: transfer of energy between objects due to T difference/change
  - Work: transfer of mechanical energy independent of T (e.g. PV) $$W = \int_{V_a}^{V_b} PdV$$
  - NO state variables
- Conservation of energy: Delta E_{int} = Q - W (main focus of this lecture!!)

Recap… Chapter 6, Heat capacity and calorimetry

- What is the relation between (sensible) heat and temperature?

- What is Calorimetry?

- Are heat capacities of gases the same at const V or at const P?

- What are the heat capacities of ideal gas?

Recap… Chapter 6, Heat capacity and calorimetry

- What is the relation between (sensible) heat and temperature?

$$Q = m \times c \times \Delta T$$

- c is the heat capacity

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  - For gas, heat capacity different for processes at constant Volume or at constant Pressure:

$$\begin{aligned} Q_{\mathrm{V}} &= nC_{\mathrm{V}}\Delta T \quad \text{volume constant} \\ Q_{\mathrm{P}} &= nC_{\mathrm{P}}\Delta T \quad \text{pressure constant} \end{aligned}$$

$$C_{\mathrm{V}} = \frac{1}{n}\left(\frac{\Delta E_{\mathrm{int}}}{\Delta T}\right)_{V=\mathrm{constant}} \equiv \frac{1}{n}\left(\frac{\partial E_{\mathrm{int}}}{\partial T}\right)_{V}$$

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$$Q_V = nC_V\Delta T \quad \text{volume constant}$$

$$Q_P = nC_P\Delta T \quad \text{pressure constant}$$

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- What are the heat capacities of ideal gas?

$$C_P - C_V = R \qquad C_V = \frac{3}{2}R$$

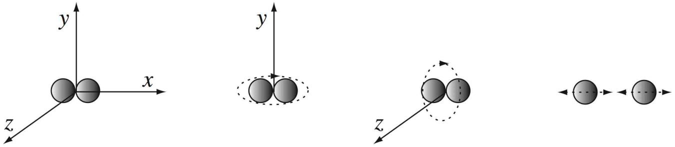
Recap… Chapter 6, Heat capacity for non-ideal gases & equipartition theorem

- If we consider non-ideal gas, which additional form of motion we should consider?

- How can we elegantly account for changes of heat capacities for non-ideal gas?

$$\frac{3}{2}R = 2.98\,\mathrm{cal/mol\cdot K},\ \frac{5}{2}R = 4.98\,\mathrm{cal/mol\cdot K},\ \frac{7}{2}R = 6.97\,\mathrm{cal/mol\cdot K}$$

Monatomic molecule: 3-translational kinetic energies, $n_f = 3$
Diatomic molecule: plus 2-rotational kinetic energies, $n_f = 5$
Diatomic molecule: plus1-vibrational kinetic and 1-vibrational potential energies, $n_f = 7$



Watch Equipartion theorem: https://www.youtube.com/watch?v=kzPHKchqkmY

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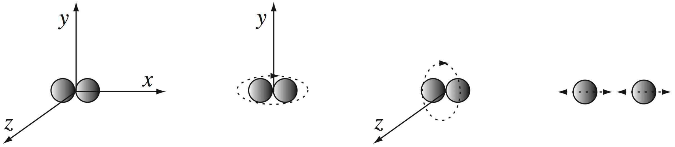

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- If we consider non-ideal gas, which additional form of motion we should consider?
  - Rotational and vibrational motions
- How can we elegantly account for changes of heat capacities for non-ideal gas?
  - Equipartion theorem: the energy of a molecule is shared equally between different degrees of freedom, each which carries on average an energy of kT/2.
  - Thus, the heat capacities (at const V, C_V) for non-ideal gas with monotomic or diatomic molecules are:

$$\frac{3}{2}R = 2.98\,\text{cal/mol}\cdot\text{K}, \quad \frac{5}{2}R = 4.98\,\text{cal/mol}\cdot\text{K}, \quad \frac{7}{2}R = 6.97\,\text{cal/mol}\cdot\text{K}$$

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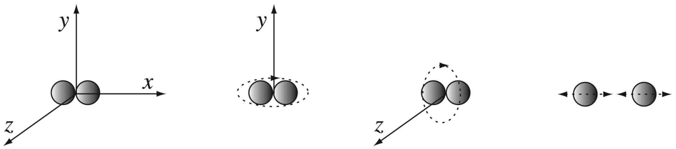

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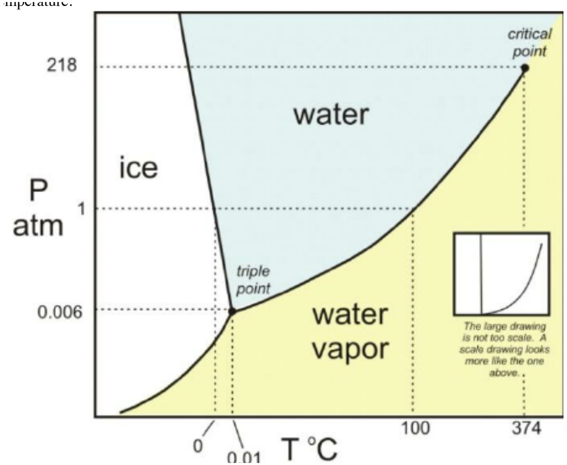
Recap… Chapter 6, Latent heat and phase transitions

- Which forms of heat do we have in TD?
- What is latent heat?
- What is a phase diagram in TD, and where comes latent heat in?
- What are the main characteristics of the phase diagram of water?



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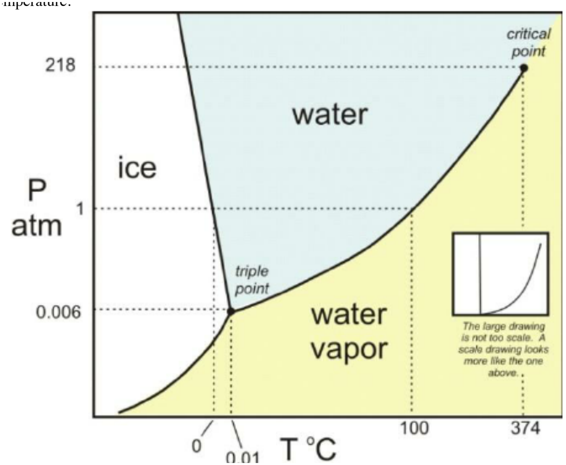

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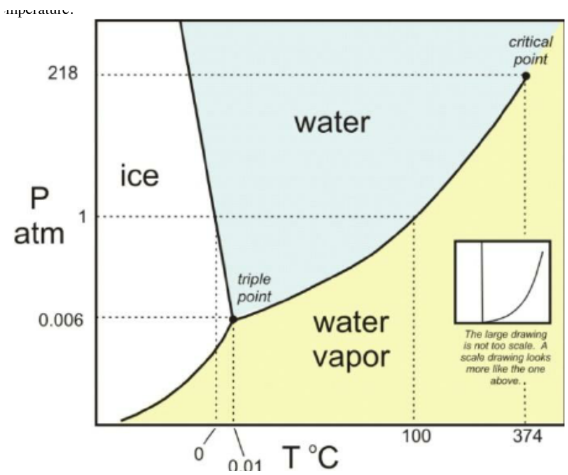

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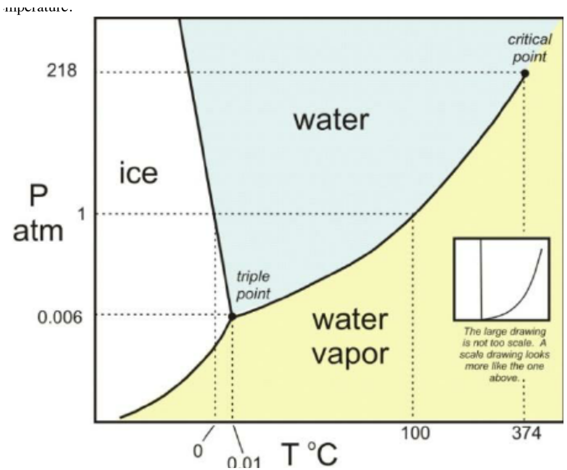

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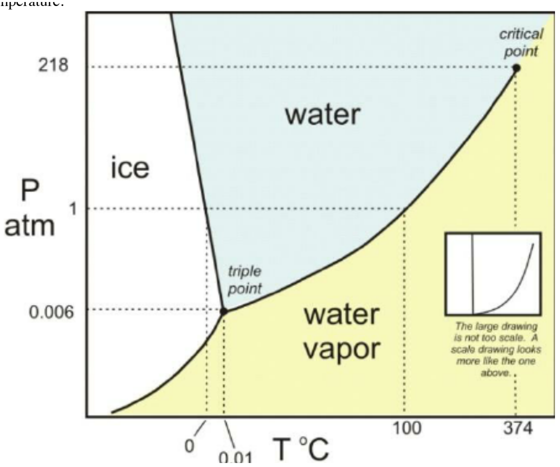
  - Unusual behaviour of water, Triple point, critical point



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Recap… Chapter 7, First law of TD

- What is the first law of Thermodynamics of a closed system?

- How is first law modified for different thermodynamic systems (other than closed)?

- Which thermal processes for gas (to change its state) do you know?

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  - isolated: no heat and work transfer, $Q = 0$, $W = 0$ —> $\Delta E_{\text{int}} = 0$
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- Which thermal processes for gas (to change its state) do you know?

Isothermal ($\Delta T = 0$): while the state changes, the temperature is kept constant.
Adiabatic ($Q = 0$): process with no heat, i.e. thermally isolated system or a very fast process.
Isobaric ($\Delta P = 0$): while the state changes, the pressure is kept constant.
Isovolumetric ($\Delta V = 0$): while the state changes, the volume is kept constant.

Recap… Chapter 7, The first law in different thermal processes

- How can we compute the internal energy for isochoric/isovolumetric $\Delta V = 0$ processes?
- How for isobaric $\Delta P = 0$ processes?
- How for isothermal $\Delta T = 0$ processes?
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Recap… Chapter 7, The first law in different thermal processes

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$$\boxed{\Delta E_{\text{int}} = Q_{\text{V}} = nC_{\text{V}}\Delta T}$$

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$$\boxed{\Delta E_{\text{int}} = nC_{\text{P}}\Delta T - P\Delta V}$$

For ideal gas: $\Delta E_{\text{int}} = nC_{\text{V}}\Delta T$

Note that here any change from one thermal state to another can be made as combinations of isochoric and isobaric processes, with $\Delta E_{\text{int}} = nC_{\text{V}}\Delta T$

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- How for isothermal **Δ**T = 0 processes?
  - $\Delta E_{\text{int}} = 0$ (if ideal gas) —> $Q = W = P\Delta V$
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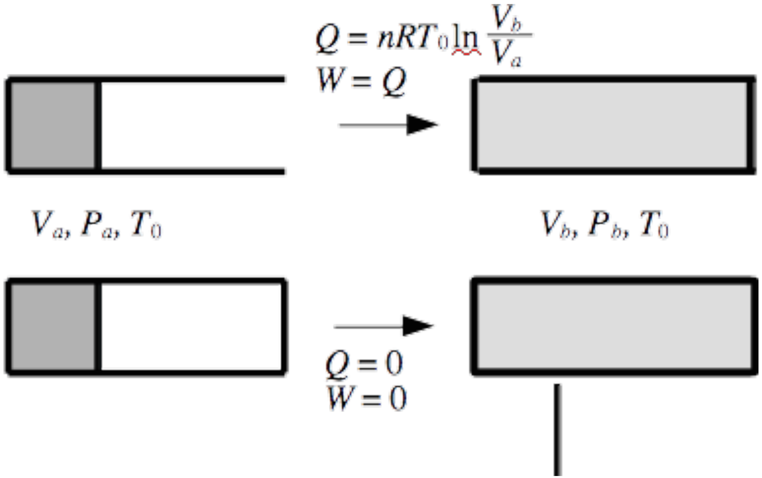
  - $\Delta E_{\text{int}} = 0$ (if ideal gas) —> $Q = W = P\Delta V$

- How for adiabatic Q = 0 processes?
  - $\Delta E_{\text{int}} = - W$
  - For ideal gas: $Q = P\Delta V + nC_V\Delta T$ —> $V^{\gamma}P = const.$ and $T\,V^{\gamma\text{-}1} = const.$

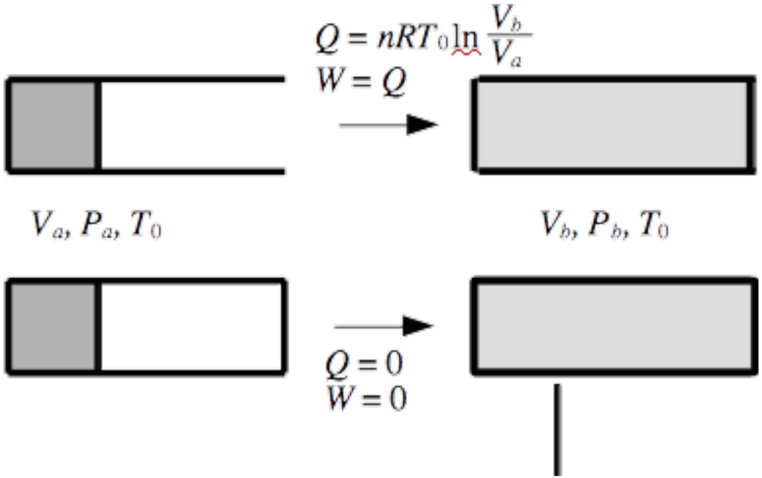
Recap Chapter 8… Reversible and irreversible processes

- What is the definition of reversible and irreversible processes?



Recap Chapter 8… Reversible and irreversible processes

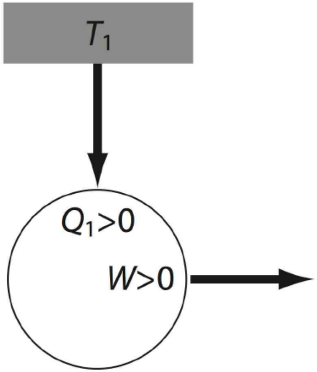
- What is the definition of reversible and irreversible processes?
    - Any process, that can be reversed by changing signs of Q and W, is reversible; Entropy production = 0.
    - Any process, that cannot be reversed by changing signs of Q and W is irreversible. “Arrow of time comes in”; Entropy production > 0



Recap Chapter 9… — Thermal machines

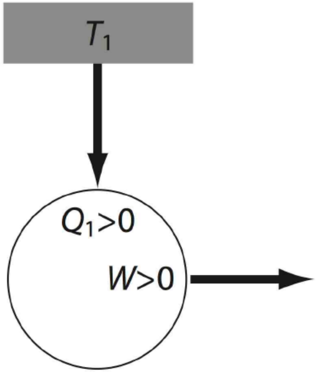
- What is a thermal machine?

- What is an equivalent formulation of 2nd law of TD?



Recap Chapter 9… — Thermal machines

- What is a thermal machine?
    - This is a TD system if it performs a heat transfer between two thermal baths
        - allowing for mechanical work being done by system on the environment and vice versa
        - by means of a machine that periodically passes though the same state (cycle of distinct processes)
- What is an equivalent formulation of 2nd law of TD?



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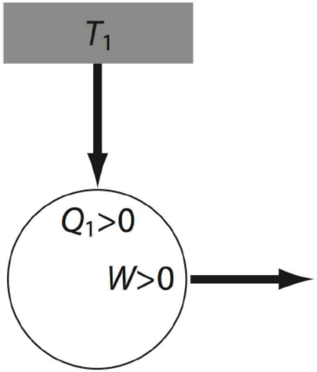
- What is an equivalent formulation of 2nd law of TD?
  - Perpetual motion machine of the 2nd kind does not exist (as Entropy change would be negative)



Recap Chapter 9 — Thermal machines

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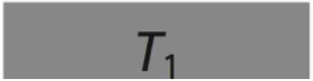
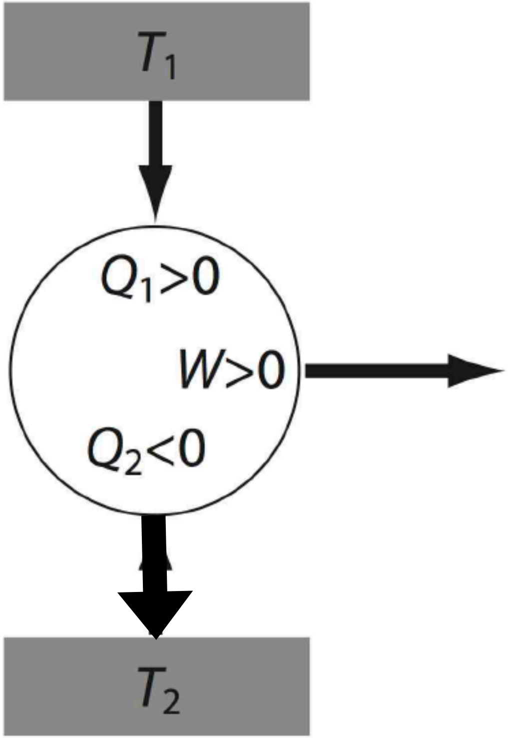


Recap Chapter 9 — Thermal machines

- What is the set up and efficiency of a thermal machine?
  - Heat taken from hot reservoir, Work conducted on environment, heat given back to cold reservoir
  - Efficiency of heat engine smaller than 1:

$$\varepsilon = \frac{W}{Q_1} = \frac{Q_1 + Q_2}{Q_1} = 1 + \frac{Q_2}{Q_1} \leq 1 - \frac{T_2}{T_1}$$

  - Best possible engine, equality for reversible processes only
  - Note that in nature most (macroscopic processes) are irreversible (friction) —> reducing epsilon



Recap Chapter 8… What is Entropy?

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- Entropy S is a state variable (independent of the path of the process), important for distinguishing between reversible and irreversible processes, quantify for “disorder”
- $dS_{system} = dS_{env} + dS_{prod}$;
    - dS_{env}: change of entropy due to heat exchange with environment
    - dS_{prod}: entropy production due to dissipation within the system

Recap Chapter 8… What is Entropy?

- Entropy S is a state variable (independent of the path of the process), important for distinguishing between reversible and irreversible processes, quantify for “disorder”
- $dS_{system} = dS_{env} + dS_{prod}$;
  - dS_{env}: change of entropy due to heat exchange with environment
  - dS_{prod}: entropy production due to dissipation within the system
- Entropy due to heat exchange with environment

$$\Delta S = \int_A^B \mathrm{d}S = \int_A^B \frac{\tilde{\mathrm{d}}Q}{T}$$

  - dS_{env} in isothermal processes

$$\Delta S_{\mathrm{ab}} = \frac{Q}{T_0} = nR\ln\frac{V_{\mathrm{b}}}{V_{\mathrm{a}}}$$

  - dS_{env} in isochoric processes

$$\Delta S_{\mathrm{ad}} = nC_{\mathrm{V}}\int_{T_0}^{T_{\mathrm{d}}}\frac{dT}{T} = nC_{\mathrm{V}}\ln\frac{T_{\mathrm{d}}}{T_0}$$

  - dS_{env} in isobaric processes

$$\Delta S_{\mathrm{db}} = nC_{\mathrm{P}}\int_{T_{\mathrm{d}}}^{T_0}\frac{dT}{T} = n\left(C_{\mathrm{V}} + R\right)\ln\frac{T_0}{T_{\mathrm{d}}}$$

  - dS_{env} in adiabatic processes is zero (as Q is zero)

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$$\Delta S = \int_A^B \frac{\tilde{\mathrm{d}}Q_{\mathrm{reversible}}}{T} > \int_A^B \frac{\tilde{\mathrm{d}}Q_{\mathrm{irreversible}}}{T}$$

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        - For irreversible processes, contribution from entropy production, irreversibly increasing the internal energy
    - Entropy production due to dissipation within a system
        - Reversible: $dS_{prod} = 0$
        - Irreversible: $dS_{prod} > 0$ (e.g. free expansion of gas at T=const and Q=0)

Recap Chapter 8 … Entropy and the three laws of Thermodynan

- How can we connect entropy to the first law of TD?

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- What is the third law of Thermodynamics?

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- What is the third law of Thermodynamics?
  - The entropy of a system converges to a constant value $S_0 = 0$ for $T \rightarrow 0$ independent of all the other properties for the particular system.

Recap Chapter 8 Statistical interpretation of entropy

- How can we interpret entropy from a microscopic/statistical point of view?

- What are then the implications of the second law of TD?

- What are the implications for the third law of TD?

- Entropy change for irreversible Joule free expansion in an thermally isolated system can be computed by a reversible, isothermal expansion:

$$\Delta S \approx nR\ln\frac{V_b}{V_a}$$

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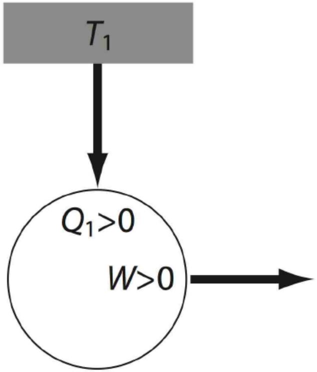
Recap Chapter 9... — Thermal machines

- What is a thermal machine?

- What is an equivalent formulation of 2nd law of TD?



Recap Chapter 9… — Thermal machines

- What is a thermal machine?
  - This is a TD system if it performs a heat transfer between two thermal baths
    - allowing for mechanical work being done by system on the environment and vice versa
    - by means of a machine that periodically passes though the same state (cycle of distinct processes)
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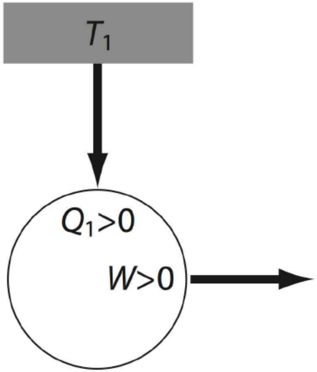

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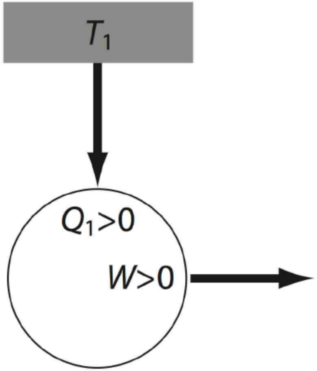
- What is an equivalent formulation of 2nd law of TD?
  - Perpetual motion machine of the 2nd kind does not exist (as Entropy change would be negative)



Recap Chapter 9 — Thermal machines

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- What is the set up and efficiency of a thermal machine?
  - Heat taken from hot reservoir, Work conducted on environment, heat given back to cold reservoir
  - Efficiency of heat engine smaller than 1:

$$\varepsilon = \frac{W}{Q_1} = \frac{Q_1 + Q_2}{Q_1} = 1 + \frac{Q_2}{Q_1} \leq 1 - \frac{T_2}{T_1}$$

  - Best possible engine, equality for reversible processes only
  - Note that in nature most (macroscopic processes) are irreversible (friction) —> reducing epsilon