Rate of Heating and Cooling

Example: Heating and cooling of Water

Heating

Cooling

Exponential decay
Newton’s Law of Cooling

- $T_S > T_E$: System S cools until it is in thermal equilibrium with E. In an isolated system $T_S$ decreases while $T_E$ increases.
- The cooling rate is following the exponential decay law also known as **Newton’s Law of Cooling**:

$$\Delta T = \Delta T_0 e^{-at}$$

( $\Delta T$ falls to 0.37 $\Delta T_0$ (37% of $\Delta T_0$) at time $t = 1/a$ )

- $\Delta T_0$ is the temperature difference at the starting point of the measurement ($t=0$), $\Delta T$ is the temperature difference at $t$
Differentiating Newton’s law of cooling

\[
\frac{d\Delta T}{dt} = -a\Delta T
\]

The rate constant \( a \) determines how fast \( \Delta T \to 0 \).

\( a \) depends on:
- convection, \( h \)
- conduction, \( k \)
- mass, \( m \)
- specific heat, \( c \)

Newton cooling law can be rewritten as

\[
\ln\left(\frac{\Delta T}{\Delta T_0}\right) = -at
\]

By plotting \( \ln\left(\frac{\Delta T}{\Delta T_0}\right) \) against \( t \) the rate constant \( a \) can be determined.
For time derivatives a "dot" is used:

\[ \Delta \dot{T} \equiv \frac{d\Delta T}{dt} = -a\Delta T \]

If we are interested in the rate of the heat released we use

\[ Q(t) = -cm\left[\Delta T_0 - \Delta T\right] \]

If we assume that \( m \) and \( c \) approximately stays constant in the cooling process we get

\[ \dot{Q} = \frac{dQ}{dt} = cm \frac{d\Delta T}{dt} = -acm\Delta T \]
Example: Cooling a cup of coffee with milk.

Question: At what time $t$ should the milk be added to cool down the coffee more efficiently?

Answer: $T_C = 94 \, ^\circ C$  ideal brewing temperature for coffee
$T_E = 21 \, ^\circ C$  room temperature
$T_D = 40 \, ^\circ C$  ideal drinking temperature of coffee
$T_M = 4 \, ^\circ C$  temperature of milk out of the fridge
$V_C = 500 \, mL$ volume of coffee
$V_M = 50 \, mL$ volume of milk
$c_M = c_C$  specific heat of milk and coffee are the same
Experiment 1: Instant mixture \((t=0)\) of water and milk

\[
Q_{\text{cold}} = -Q_{\text{hot}} \quad \Rightarrow \quad c_M m_M \Delta T_M = -c_C m_C \Delta T_C \quad \Rightarrow \quad m_M (T_M - T) = -m_C (T_C - T)
\]

\[
T = \frac{m_M T_M + m_C T_C}{m_M + m_C}
\]

\[
T = \frac{0.5\text{kg} \times 94^\circ\text{C} + 0.05\text{kg} \times 4^\circ\text{C}}{0.5\text{kg} + 0.05\text{kg}} = 85.81^\circ\text{C}
\]

Experiment 2: Milk is added at \(t_1 > 0\) such that \(T=T_D\) at \(t_1\).

Temperature of coffee at mixture time \(t_1\):

\[
T_C(t_1) = \frac{m_M (T_D - T_M) + m_C T_D}{m_C} = 43.6^\circ\text{C}
\]

The question now is whether water cools faster from \(85.81^\circ\text{C}\) to \(40^\circ\text{C}\) or from \(94^\circ\text{C}\) to \(43.6^\circ\text{C}\)
Newton’s Law

\[ T(t) = T_E + (T_i - T_E)e^{-at} \implies t = -\frac{1}{a} \left[ \ln(T - T_E) - \ln(T_i - T_E) \right] \]

We do not know the rate constant \( a \), therefore we use \( (T_E = 20^\circ C) \)

Exp.1: \[ t_1 = -\frac{1}{a} \left[ \ln(T_1 - T_E) - \ln(T_{1,i} - T_E) \right] \]
\[ T_{1,i} = 85.8 \text{ } ^\circ \text{C} \]
\[ T_1 = 40.0 \text{ } ^\circ \text{C} \]

Exp.2: \[ t_2 = -\frac{1}{a} \left[ \ln(T_2 - T_E) - \ln(T_{2,i} - T_E) \right] \]
\[ T_{2,i} = 90.0 \text{ } ^\circ \text{C} \]
\[ T_2 = 43.6 \text{ } ^\circ \text{C} \]

where 1 and 2 stands for experiment 1 and 2. We divide both equations:

\[ \frac{t_1}{t_2} = \frac{\left[ \ln(T_1 - T_E) - \ln(T_{1,i} - T_E) \right]}{\left[ \ln(T_2 - T_E) - \ln(T_{2,i} - T_E) \right]} = 1.046 \]

Therefore \( t_1 > t_2 \) and experiment 2 is about 4.6% faster.
Higher temperature in a gas translates into higher kinetic energies of the gas atoms or molecules. Molecules in the gas phase undergo translational, rotational and vibrational motions, which are described by quantum theory.

**Translational motion**

- $E_{\text{kin}}$
The Ideal Gas

- For gases, the interatomic forces within the gas are very weak.
  - We can imagine these forces to be nonexistent

- Note that there is no equilibrium separation for the atoms or molecules
  - Thus, no “standard” volume at a given temperature, a gas expands. For a gas, the volume is entirely determined by the container holding the gas.

- The equation that interrelates these quantities is called the equation of state
The equation of state for an ideal gas

\[ PV = nRT \]

This is known as the **ideal gas law**

- \( R \) is a constant, called the **Universal Gas Constant**
  - \( R = 8.314 \text{ J/mol K} = 0.08214 \text{ L atm/mol K} \)
- 1 mole of any gas at 1 atm and 0\(^{\circ}\) C is 22.4 L
- The ideal gas law is often expressed in terms of the total number of molecules, \( N \), present in the sample

\[ PV = nRT = (N/N_A)RT = Nk_BT \]

- \( k_B = 1.38 \times 10^{-23} \text{ J/K} \) is the **Boltzmann constant**
- \( N_A = 6.023 \times 10^{23} \text{ mol}^{-1} \) is **Avogadro’s constant**
The molecules obey Newton’s laws of motion, but as a whole they move randomly.

- Any molecule can move in any direction with any speed
- At any given moment, a certain percentage of molecules move at high speeds
- Also, a certain percentage move at low speeds

The molecules interact only by short-range forces during elastic collisions.

The molecules make elastic collisions with the walls.

The gas under consideration is a pure substance.

- All molecules are identical
An ideal gas is often pictured as consisting of single atoms.

Molecular rotations and vibrations have no effect, on average, on the motions considered.

In a real gas all these assumptions are not valid anymore. However, the behavior of molecular gases approximate that of ideal gases quite well.
The Non-ideal Gas

- The isotherms of a real gas: Isopentane

- For an ideal gas the compressibility \( Z \) is exactly 1.0 at all pressures and temperatures:

\[
Z = \frac{pV_m}{RT} = 1
\]

\[
V_m = \frac{V}{n}
\]

molar volume
The **compressibility** of Ar

\[ Z = \frac{pV_m}{RT} \]
Attractive and repulsive regions due to intermolecular forces

Energy [eV]

Distance [Å]

Van der Waals interactions

Attractive

Repulsive
The equation of state for a real gas

\[ PV_m = RT \left( 1 + B(T)/V_m + C(T)/V_m^2 + D(T)/V_m^3 + \ldots \right) \]

\[ PV_m = RT \left( 1 + B'(T)/P + C'(T)/P^2 + D'(T)/P^3 + \ldots \right) \]

The equations are simple Taylor expansions in \( V_m \) or \( P \)

The temperature dependent coefficients \( B(T) \), \( C(T) \) etc. are called **virial coefficients**

\( B(T) \) is the second virial coefficient, \( C(T) \) the third virial coefficient etc. These coefficients are often used as constants, i.e. \( B(T) = B \) and \( C(T) = C \)

For both equations the virial coefficients are approximately related to each other

\[ B' = \frac{B}{RT} \quad \quad C' = \frac{C - B^2}{(RT)^2} \]
## Second Virial Coefficients $B(T)$

<table>
<thead>
<tr>
<th></th>
<th>100 K</th>
<th>273 K</th>
<th>373 K</th>
<th>600 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>11.4</td>
<td>12.0</td>
<td>11.3</td>
<td>10.4</td>
</tr>
<tr>
<td>Ar</td>
<td>-187.0</td>
<td>-21.7</td>
<td>-4.2</td>
<td>11.9</td>
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<tr>
<td>N$_2$</td>
<td>-160.0</td>
<td>-10.5</td>
<td>6.2</td>
<td>21.7</td>
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<tr>
<td>O$_2$</td>
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<td>-22.0</td>
<td>-3.7</td>
<td>12.9</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>-149.7</td>
<td>-72.2</td>
<td>-12.4</td>
<td></td>
</tr>
</tbody>
</table>

He is pretty much an ideal gas!
Kinetic gas theory

Microscopic World

$\{x_i, v_i, m_i, \ldots\}$

Macroscopic World

$P, V, T, n$
Assume a container is a cube of length $d$ (e.g. unit length 1m)

Look at the motion of the molecule in terms of its velocity components

Look at its momentum and the average force

Assume perfectly elastic collisions with the walls of the container

The relationship between the pressure and the molecular kinetic energy comes from momentum and Newton’s Laws
The relationship between pressure and kinetic energy

\[ P = \frac{2}{3} \frac{N}{V} \left( \frac{1}{2} \overline{mv^2} \right) = \frac{2}{3} \frac{N}{V} \overline{E_{\text{kin}}} \]

This tells us that pressure is proportional to the number of atoms / molecules per (unit) volume \((N/V)\) and to the average translational kinetic energy of the atoms / molecules

The derivation of this formula is given in the textbook
This equation also relates the **macroscopic quantity** of pressure with a **microscopic quantity** of the average value of the square of the molecular speed.

One way to increase the pressure is to increase the number of molecules per unit volume.

The pressure can also be increased by increasing the speed (kinetic energy) of the molecules.

We can take the pressure as it relates to the kinetic energy and compare it to the pressure from the equation of state for an ideal gas.

\[
P = \frac{2}{3} \frac{N}{V} \left( \frac{1}{2} m \langle v^2 \rangle \right) = \frac{2}{3} \frac{N}{V} \bar{E}_{kin} = \frac{N}{V} k_B T
\]

Therefore, the **temperature is a direct measure of the average molecular kinetic energy**!
Simplifying the equation relating temperature and kinetic energy gives

\[ \frac{1}{2} mv^2 = \frac{3}{2} k_B T \]

This can be applied to each direction, e.g. for a single atom or molecule

\[ \frac{1}{2} mv_x^2 = \frac{1}{2} k_B T \]

with similar expressions for \( v_y \) and \( v_z \) and

\[ \frac{1}{2} mv_x^2 + \frac{1}{2} mv_y^2 + \frac{1}{2} mv_z^2 = \frac{1}{2} mv^2 = \frac{3}{2} k_B T \]
Each translational degree of freedom contributes an equal amount to the energy of the gas.

- In general, a degree of freedom refers to an independent means by which a molecule can possess energy.

A generalization of this result is called the theorem of equipartition of energy.

- Each degree of freedom contributes $\frac{1}{2} k_B T$ to the energy of a system, where possible degrees of freedom in addition to those associated with translation arise from rotation and vibration of molecules.
The total kinetic energy is just $N$ times the kinetic energy of each molecule

$$E_{\text{tot kin}} = N \left( \frac{1}{2} m \bar{v}^2 \right) = \frac{3}{2} N k_B T = \frac{3}{2} nRT$$

If we have a gas with only translational energy, this is the internal energy of the gas!

This tells us that the internal energy of an ideal gas depends only on the temperature

The root mean square ($rms$) speed is the square root of the average of the squares of the speeds

- Square, average, take the square root

Solving for $v_{rms}$ we find

$$v_{rms} = \sqrt{\frac{\sum v_i^2}{N}} = \sqrt{\bar{v}^2} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}}$$

$M$ is the molar mass and $M = mN_A$
At a given temperature, lighter molecules move faster, on the average, than heavier molecules because of the mass $m$

<table>
<thead>
<tr>
<th>Some $v_{rms}$ speeds</th>
<th>$Molar mass$ (g/mol)</th>
<th>$v_{rms}$ at 20°C (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td>2.02</td>
<td>1902</td>
</tr>
<tr>
<td>He</td>
<td>4.00</td>
<td>1352</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>18.0</td>
<td>637</td>
</tr>
<tr>
<td>Ne</td>
<td>20.2</td>
<td>602</td>
</tr>
<tr>
<td>$N_2$ or CO</td>
<td>28.0</td>
<td>511</td>
</tr>
<tr>
<td>NO</td>
<td>30.0</td>
<td>494</td>
</tr>
<tr>
<td>$O_2$</td>
<td>32.0</td>
<td>478</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>44.0</td>
<td>408</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>64.1</td>
<td>338</td>
</tr>
</tbody>
</table>

$$v_{rms} = \sqrt{\frac{3k_B T}{m}}$$