Enzymes are proteins that catalyze (i.e., increase the rate of) chemical reaction.

Interconvert carbon dioxide and bicarbonate to maintain acid-base balance in blood and other tissues, and to help transport carbon dioxide out of tissues.

\[
\text{CO}_2 + \text{H}_2\text{O} \xrightarrow{\text{Carbonic anhydrase}} \text{H}_2\text{CO}_3
\]  
(in tissues with high CO\textsubscript{2} concentration)

\[
\text{H}_2\text{CO}_3 \xrightarrow{\text{Carbonic anhydrase}} \text{CO}_2 + \text{H}_2\text{O}
\]  
(in lungs with low CO\textsubscript{2} concentration)

In humans the process works nicely. Can we understand how does it work?

Increasing the rate of chemical reaction is the dream of industry.
Oxidation of methane to methanol

The methane oxidation is a difficult and expensive reaction because the methane is the most inert hydrocarbon (C-H bond is one of the most strong)

but

Methanotrophs bacteria use methane monooxygenase (MMO) enzymes to convert methane to methanol at ambient conditions !!!
MOO metal centers. (A) Mononuclear copper center. (B) Dinuclear copper center. (C) Zinc center. Oxygen atoms are colored red; nitrogen atoms are colored blue; Zinc atom in grey

Oxidation at the dinuclear copper center


Copper edge EXAFS data and simulations for MMO
XAS (XANES)

Photo Emission

Absorption coefficient, $\alpha$

Photon energy, $h\nu$ (eV)

Outgoing wave

$|f_0\rangle$

$\mu$

$E_0$

Outgoing + backward scattered wave

$|f_0\rangle = |f_0\rangle + |\delta f\rangle$

$\mu$

$E_0$

V.L. Aksenov  Physics of Particles and Nuclei, 32, No. 6, 1–33 (2001)
EXAFS: Extended X-rays absorption fine structure

**Principle:**
1) photon in - electron out
2) The emitted electron (described by a wave) is diffused by the neighboring atoms
3) Interference between emitted and diffused wave
4) The absorption depends on the interference

The interference between emitted and diffused wave is constructive or destructive depending on:

1) The distance between the absorbing and diffusing atoms -> information on the crystallographic structure
2) The reflection coefficient of the diffusing atom -> information on the chemical environment
3) The wavelength of the emitted electron -> \( E_{\text{kin}} = h\nu - E_{\text{edge}} = \frac{h^2 k^2}{2m} = \frac{h^2}{2m\lambda^2} \)
\[ \lambda = \frac{h}{2m(h \nu - E_K)^{1/2}} \]

Interference conditions depend on the in-coming photons

EXAFS expression

\[ k \chi(k) = k \left( \frac{\mu(k) - \mu_0(k)}{\mu_0(k)} \right) = \sum_i S_0^2 N_i(\varepsilon)/R_i^2 A_i(k) \exp(-2R_i/\lambda(k)) \exp(-2k^2\sigma_i^2) \sin(2kR_i + 2\delta_i + \phi_i) \]

Amplitude factor

Attenuation factor: reduced electronic mean free path \( \lambda \)

Debye-Waller term: thermal vibrations and crystallographic disorder

Phase factor

\( kR_i \) -> phase due to the distance between absorbing and diffusing atom
\( \delta_i \) -> phase due to the propagation in the potential of the absorbing atom
\( \phi_i \) -> phase due to the propagation in the potential of the diffusing atom
\( \mu_0(k) \) is the atomic background

\( k \chi(k) \) is a summation over sinusoid functions

The Fourier transform of \( k\chi(k) \) gives information on the phase factor i.e. on the atomic distances.
Present interest in chalcogenide glasses is driven by the ability of a particular composition (Ge$_2$Sb$_2$Te$_5$, or GST) to be repeatedly switched between crystalline ($c$) and amorphous ($a$) states by application of light or electrical pulses of suitable intensities and durations. Differences in the properties of the $a$ (matt) and $c$ (transparent) materials (e.g., reflectivity) allows for device applications.

**Fragments of the local structure of GST around Ge atoms in the crystalline (left) and amorphous (right) states.** Stronger covalent bonds are shown as thicker lines whereas weak interblock bonds are shown as thinner lines.

**The crystal structure of laser-amorphized GST.** A schematic twodimensional image of the lattice distortion of the rocksalt structure due to charge redistribution between the constituent elements; atoms that form the building block of the GST structure are shown using thick lines. The arrows indicate displacements of atoms from the ideal rocksalt positions.
Spectra measured at the K-edges of: Ge, Sb and Te. On amorphization the bonds become shorter (as shown by shifts in the peak positions) and stronger, that is, more locally ordered (as shown by increases in the peak amplitudes and concurrent decreases in the peak widths).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond length (Å) From EXAFS</th>
<th>Bond length (Å) From XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge–Te</td>
<td>2.83 ± 0.01</td>
<td>3.0(1) ± 0.3</td>
</tr>
<tr>
<td>Sb–Te</td>
<td>2.91 ± 0.01</td>
<td>3.0(1) ± 0.3</td>
</tr>
<tr>
<td>Te–Te (2nd)</td>
<td>4.26 ± 0.01</td>
<td>4.2(6) ± 0.2</td>
</tr>
<tr>
<td>Ge–Te</td>
<td>2.61 ± 0.01 (Laser-amorphized)</td>
<td>2.61*</td>
</tr>
<tr>
<td>Sb–Te</td>
<td>2.85 ± 0.01</td>
<td></td>
</tr>
</tbody>
</table>
How I can find the lattice parameters?
c-axis change from particle to particle -> diffraction does not work
The best agreement assuming:

(40 ± 8) atom % Fe around the Pt atoms and (70 ± 12) atom % Fe around the Fe atoms and a lattice constant of (0.387 ± 0.004) nm.

For FePt bulk material a lattice constant of (0.383 ± 0.003) nm.

Magnetism strongly depends on the crystallographic structure.
XANES: X-ray Absorption Near Edge Structure

The absorption edge shape is representative of the film chemical composition

$$\text{SiO}_2 / \text{Ni}_{81}\text{Fe}_{19}(80 \text{ Å}) / \text{Co}(20 \text{ Å}) / \text{Al}(20 \text{ Å} + \text{plasma oxidation for } x \text{ seconds}) / \text{Ni}_{18}\text{Fe}_{19}(100 \text{ Å}) / \text{Cu}(30 \text{ Å})$$

Satellite peak due to the CoO

Catalysis and catalysts

A catalyst is a substance that increases the rate of a reaction

Gold particles as a catalyst: CO + O₂ -> 2CO₂

(a-c) Au20 island with coadsorbed O₂ and CO (C atom in gray online): (a) the initial configuration; (b) the transition state (c) formation and desorption of CO₂; (d) the total energy profile along the C-O(2) reaction coordinate.

A. T. Bell, Science, 299, 1688 (2003);
M. Valden et al., Science, 281, 1647 (1998);
C. Zhang et al., J. Am. Chem. Soc., 129, 2228 (2007);
Exposing the Au + O₂ to CO produces first the CO + O₂ → CO₂ and then the Au + CO bonding formation.
**Bremsstrahlung** is the electromagnetic radiation produced by the acceleration of a charged particle, such as an electron.

The electromagnetic field generated by a particle of charge $q$ subjected to an acceleration $a$ is described (at large distance $R$) by:

$$\mathbf{E} = \frac{q}{4\pi\varepsilon_0 c^2 R} \frac{1}{(1 - n \cdot v/c)^3} \mathbf{n} \wedge [(\mathbf{n} - \mathbf{v}/c) \wedge a]$$

$$\mathbf{B} = (\mathbf{n} \wedge \mathbf{E})/c$$

Poynting’s vector: $\Sigma = 1/\mu_0 \mathbf{E} \wedge \mathbf{B}$

$$|\Sigma| \propto |\mathbf{n} \wedge [(\mathbf{n} - \mathbf{v}/c) \wedge a]|^2 \frac{1}{(1 - n \cdot v/c)^6}$$

The larger is $|a|$ the larger the intensity of the emitted radiation.

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The larger is $|a|$ the larger the intensity of the emitted radiation.
Electrons emitted by an electron gun are first accelerated in a linear accelerator (linac) and then transmitted to a circular accelerator (booster synchrotron) where they are accelerated to reach an energy level of 6 GeV.

$$E = \frac{m_0c^2}{\sqrt{1 - \beta^2}} \quad \beta = 0.9999$$

These high-energy electrons are then injected into a large storage ring (844 meters in circumference) where they circulate in a vacuum environment, at a constant energy, for many hours.
The synchrotron beams emitted by the electrons are directed towards the "beamlines" which surround the storage ring in the experimental hall. Each beamline is designed for use with a specific technique or for a specific type of research. Experiments run throughout the day and night.
**Undulator**: The elliptical undulator is a device for the production of circularly polarized synchrotron radiation. In an EPU, the magnetic field vector rotates as a particle passes through the device, causing the particle to spiral about a central axis. EPUs consist of four banks of magnets—two on top and two below. The peak energy of the undulator output is changed by varying the vertical separation between the magnet assemblies, a so-called ‘gap scan’, while the polarization is varied by changing the relative positions (phases) of adjacent rows of magnets—a ‘row scan’.

![Magnets and particle path in an EPU.](image)

**Monochromator**: an optics consisting of mirror and gratings select the photon energy -> $\Delta E/E < 10^{-3}$

**Intensity**: more than $10^{12}$ photons/second

For comparison a Mg K$_{\alpha}$ XPS laboratory source produces an intensity of $10^7$ photons/second

**Acquisition time**: 1 second vs 30 hours for comparable signal to noise ratio
Synchrotron light spectrum

SLS: Swiss Light Source

You can choose the photon energy you want

Convention:

Soft X-rays \(\rightarrow\) energy \(<\) 1keV
Hard X-rays \(\rightarrow\) energy \(\geq\) 1keV
The electrons passing in the undulator start to oscillate and emit radiation. If the synchrotron radiation becomes sufficiently strong, the transverse electric field of the radiation beam interacts with the transverse electron current created by the sinusoidal wiggling motion. The electrons are thus clumped in microbunches, separated by one optical wavelength along the axis. The bunched electrons emit sub-picosecond pulses of coherent radiation.
Intenisty: $10^{12}$ photons/pulse
Wave length 0.1 - 10 nm
Pulse length: 20 fs
Pulse energy: 0.1 mJ
Beam radius: 50 µm
Repetition rate: 100 Hz

Time dependent (femtosecond) experiments at the atomic scale
Ultrafast magnetization dynamics at the nanoscale

Time constants for equilibration and interaction of the reservoirs. Models may be clarified with ultrafast pump-probe experiments at the Swiss-FEL.
Time and length scales for chemical and biochemical processes

- Dynamics of protein folding and catalytic action
- Real time chemistry

https://www.psi.ch/swissfel/ultrafast-biochemistry