Many atom systems, Ideal Gases

The model of an ideal gas is thought of as a **large number** (*N*) **of spherical particles with identical masses moving randomly**, while colliding completely elastically with each other and the walls of the container. All other **interactions**, and **the total volume of the molecules** relative to the size of the container **can be ignored**

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$$

(The averaging is denoted by a bar – this has to be done after calculating squares.)
These formulae can also be considered as one definition of **temperature**. In this model, the **pressure of the gas** originates in the collision of particles with the container.

$$pV = NkT$$

Real Gases

we have to **take into account**
1. **the intrinsic volumes of the molecules,** and that the
2. **molecules** (approaching the wall) before collision slightly **slowed down by the attraction of others**

if the volume of a single molecule is denoted by b: $p(V-Nb) = NkT$

Applying this correction we would get smaller pressure due to the attraction effect mentioned above.

The negative correction depends on the attraction by other particles on a molecule approaching the wall, and the number of molecules hitting the wall per unit time. Both are proportional to the number of molecules per unit volume, $n = N/V$.

Thus

$$p = \frac{NkT}{V - Nb} - an^2$$

where a is a constant specific for the substance, and indicative of the strength of intermolecular forces
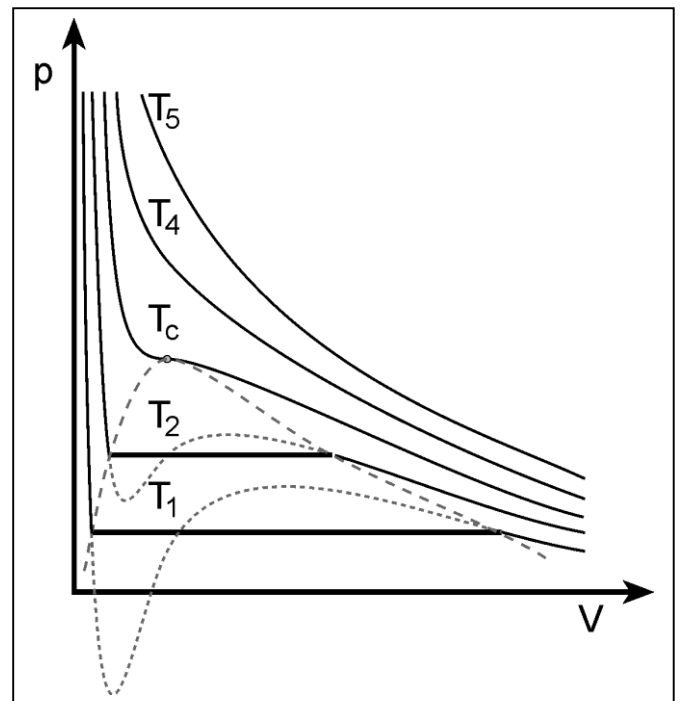
Van der Waals state equation

for real gases:

$$\left(p + a\frac{N^2}{V^2} \right)(V - Nb) = NkT$$

Van der Waals isotherms ($p(V)$ diagram; $T_1 < T_2 < T_c < T_4 < T_5$).
(Inside the dashed line both phases (liquid and vapor) are present.)

In order to liquefy a gas, it must be cooled under the so-called critical temperature (T_c).

Boltzmann distribution

In a system of thermal equilibrium (constant temperature) the total energy (E) is distributed in such a way that **an average of ½ kT energy corresponds to each degree of freedom** (equipartition theorem)

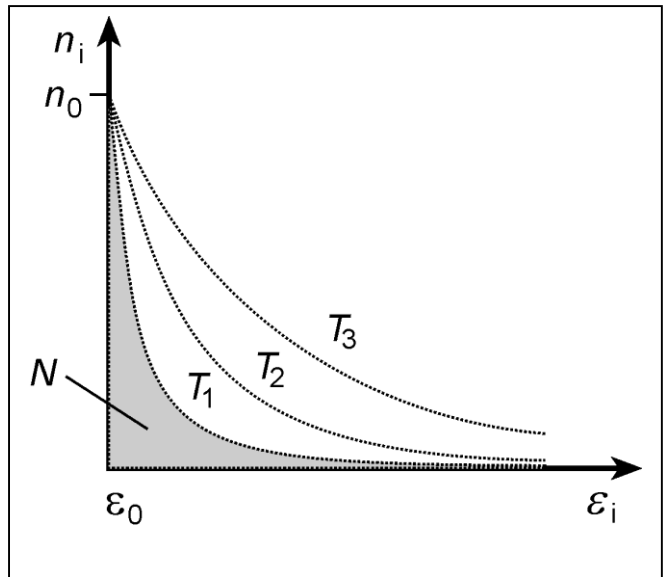energy is constantly being redistributed among all particles and degrees of freedom.

we could specify only the distribution of energy, by determining the numbers of particles (n_0, n_1, n_2, …) with energies (ε_0, ε_1, ε_2, …) **A series of occupation numbers $\{n_0, n_1, n_2, …\} = \{n_i\}$ define state of the system**.

in thermal equilibrium there is a series $\{n_i\}$ with the highest probability

$$E = \sum_i n_i \varepsilon_i, \quad N = \sum_i n_i$$

$$n_i = n_0 e^{-\frac{\varepsilon_i - \varepsilon_0}{kT}}$$

Graphical representation of the Botzmann distribution at various temperatures ($T_3 > T_2 > T_1$)

Phenomena based on Boltzmann distribution

a) The barometric formula

It is generally known that atmospheric density decreases with altitude. The density of the gas is given by the number of molecules per unit volume ($n=N/V$).

$$\varepsilon_{pot} = mgh$$

$$\frac{n(h)}{n(0)} = e^{-\frac{mgh}{kT}}$$

b) *Thermal emission of metals* (electrons emitted due to heat)

delocalized electrons of common orbits in metals behave in many aspects like gases

The higher the temperature of the metal, the more electrons can leave the metal.

Their numbers are also determined by the Boltzmann distribution.

c) *Nernst equation*

voltage of U between points A and B

$\varepsilon_{pot} = q_e U$ (q_e is the elementary charge unit)

In thermal equilibrium the occupation numbers are given by the Boltzmann distribution:

$$\frac{n_A}{n_B} = e^{-\frac{qU}{kT}} \qquad \frac{kT}{q} \ln \frac{n_A}{n_B} = U$$

This rule is analogous to the Nernst equation.

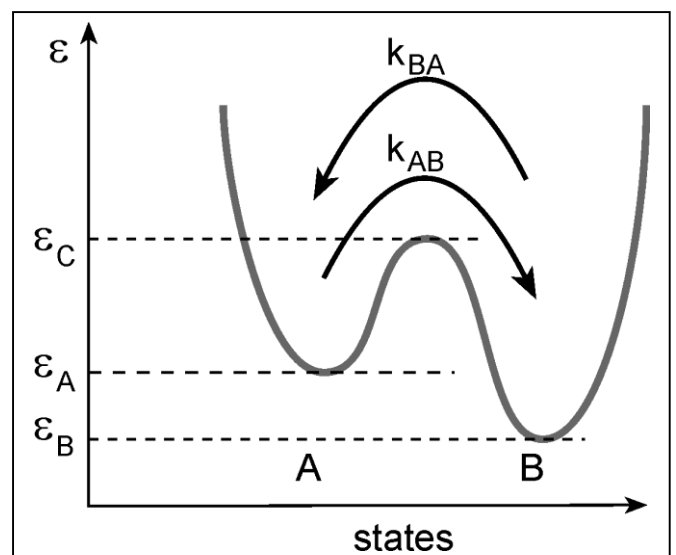## d) *Equilibrium and rates of chemical reactions*

In equilibrium, the distribution of the two states is given by:

$$\frac{n_A}{n_B} = e^{-\frac{\varepsilon_A - \varepsilon_B}{kT}}$$

The ratio $n_A/n_B = K$ is called the equilibrium constant.
reaction requires a certain amount of activation energy, which depends on the size of the energy barrier (ε_C)

therefore for the reaction rates:

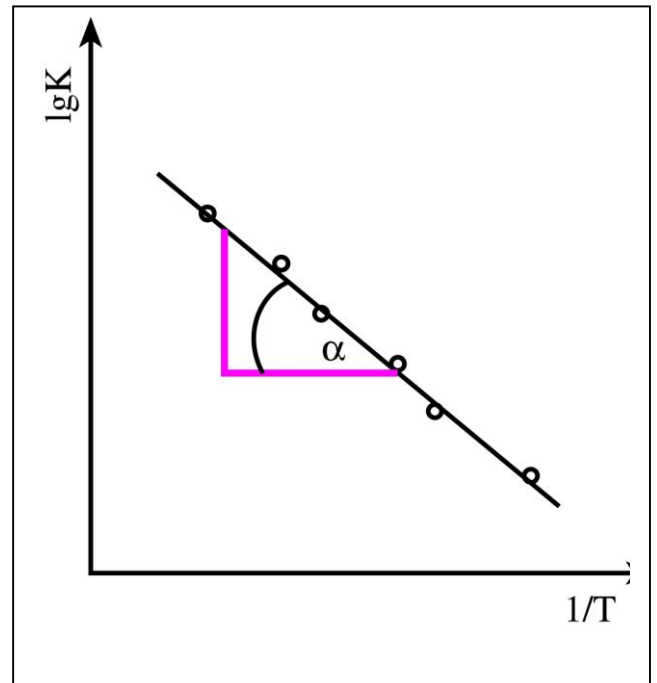$$k_{AB} = \text{const. } e^{-\frac{\varepsilon_C - \varepsilon_B}{kT}}$$

$$k_{BA} = \text{const. } e^{-\frac{\varepsilon_C - \varepsilon_A}{kT}} \qquad \text{and}$$

$$\frac{k_{AB}}{k_{BA}} = K$$

Arrhenius plot

The energy difference of the states can be obtained from the slope of the line fitted to the measurement data:

5

Solid State Materials

Crystalline States
most important property is **large-scale periodic order**
(highest level of order)

Ideal crystals are an infinite periodic spatial sequence of identical structural elements. The geometric properties and the symmetry of the crystal is **defined by the lattice** (the crystal structure is made by putting the right 'building blocks' into the lattice at each vertex). The lattice consists of basic units called **elementary cells**.
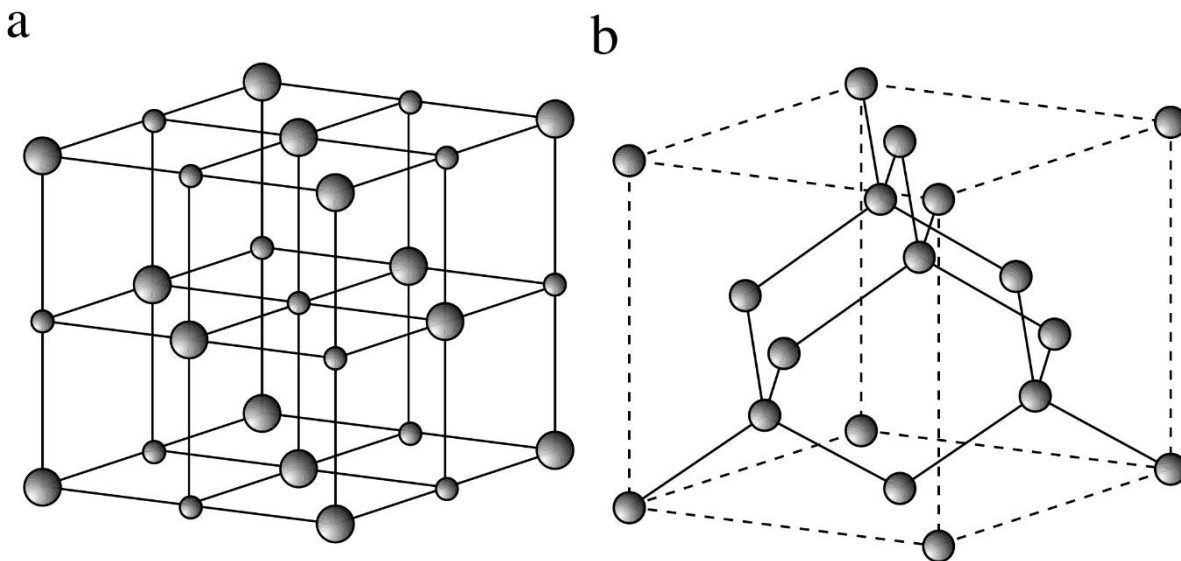

Fig. I.28. Elementary cells of NaCl (a) and Si (b) crystals.

Classification:
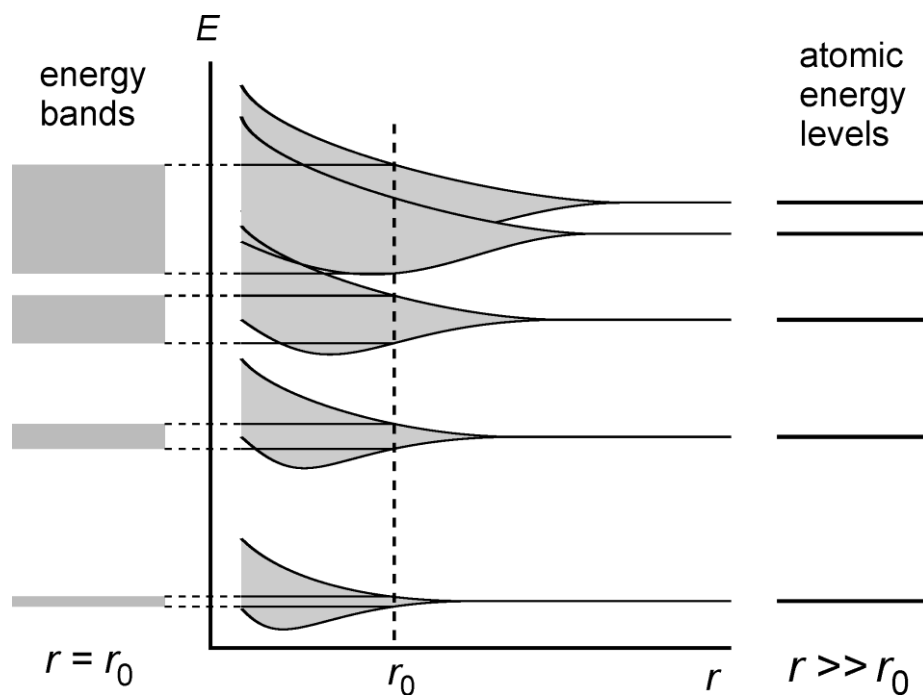**atomic, ionic, metallic, molecular lattice**

crystalline order in reality **usually only extends to microscopic scales: microcrystals, monocrystals**

Crystals are **anisotropic** substances, i.e. **they have distinguishable directions**. This can manifest, for instance, in the fact that within the crystal, light propagates with different velocities in different directions.

Energy Bands

As soon as the atoms get closer to form a crystal, and the state functions of atomic electrons start to overlap, **the Pauli principle comes into effect**. The tendency of the system to avoid identical quantum states is realized through **the 'splitting up' of the equal energies of interacting electrons into N close levels.**
As N **is very large**, the **multitude of close split levels forms in practice a continuous energy band.**

The formation of energy bands in crystals. Due to the decrease of atomic distances (r), the atomic energy levels are split up, and energy bands will form (r_0 denotes the equilibrium distance).
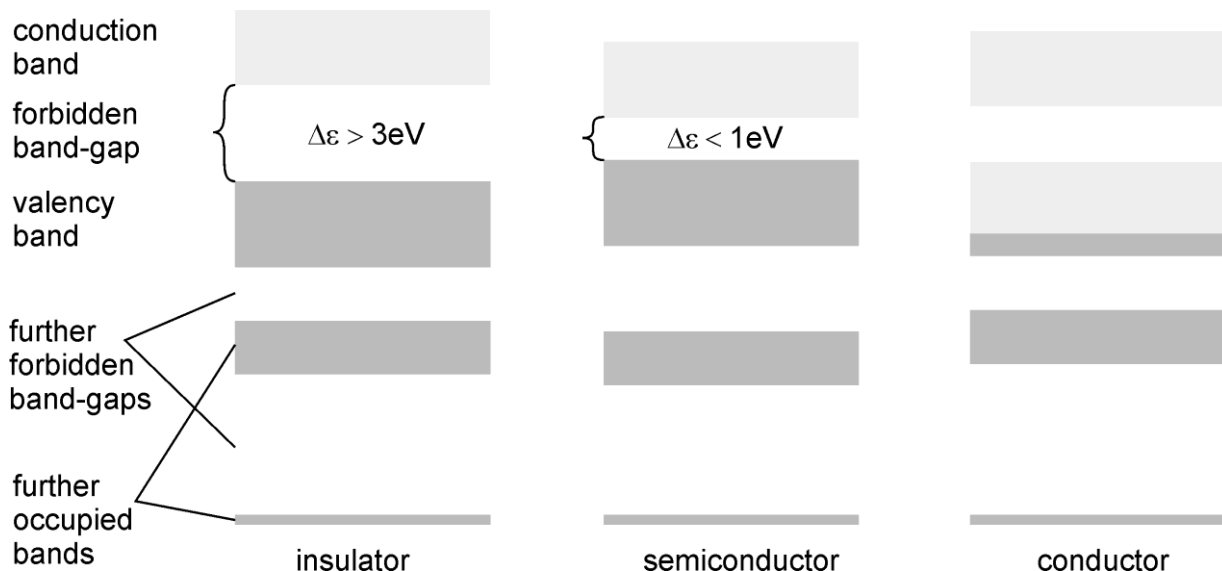
Energy Bands (continue)

As the interaction is most significant for the outmost, valence electrons, splitting happens to the greatest extent here as well. This band is called the **valence band.**
The gaps without possible energies between consecutive bands are called **forbidden band-gaps.**
Two bands may broaden to such an extent that the forbidden band-gap between them disappears completely.

If there are electrons in each energy state within the valence band, i.e. the band is 'completely occupied', then energy can only be absorbed if a minimum amount of energy corresponding to the width of the next forbidden band-gap is available.
The empty band of allowed states is called **the conduction band.**

conduction band

forbidden band-gap

$\Delta\varepsilon > 3eV$

$\Delta\varepsilon < 1eV$

valency band

further forbidden band-gaps

further occupied bands

insulator   semiconductor   conductor

The band structure of insulators, semiconductors and conductors. Occupied bands, their occupied sections are shown with darker gray and unoccupied sections with lighter gray. The blank parts in between depict the forbidden band-gaps

Properties Determined by the Width of the Forbidden Band-Gap

If $\Delta\varepsilon$ is of the order of a few eV, then the substance is an **insulator** at room temperature; if it is only a few tenths of eV, then it is a pure **semiconductor**.

Conductivity, however, is not only **affected** by the number of mobile electrons in the conduction band, but **also by** that of the electron vacancies, i.e. **holes** in the valence band.

Holes are also commonly called *p*-**type** (positive) **charge carriers**, as the counterpart of **electrons**, being *n*-**type** (negative) charge carriers.

Conductivity may also appear in the valence band, if it is not completely occupied.
These materials are **proper conductors**.

Partial occupancy may be realized in several ways: one possibility is that **the outermost electrons of the interacting atoms did not have completely occupied electron orbits originally** (as is the case with Li); another would be **an overlap of a saturated and an empty band** during the broadening of energy levels (such is the case with Na).

Optical properties:
Insulators with a forbidden band-gap wider that 3 eV are **transparent.**

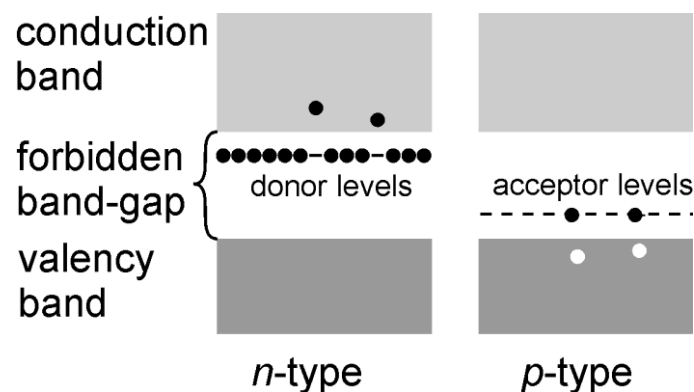# Creating 'Semiconductor Properties' by Doping

From a practical point of view (**electronics,** transistor), so-called doped or extrinsic semiconductors have major importance.
Adding small amounts of certain foreign substances (a process known as **doping**) into a pure semi-conductor crystal lattice with a completely occupied valence band results **in the creation of new electron states** that provide the material with properties of a **semiconductor with a very narrow forbidden band-gap**.
The crystal structure of Si is shown in the figure (above).
If a doping atom has a valence of five (such as P), then after forming four covalent bonds, the remaining fifth electron will occupy a loosely bound electron state in the forbidden band-gap called **donor level**.
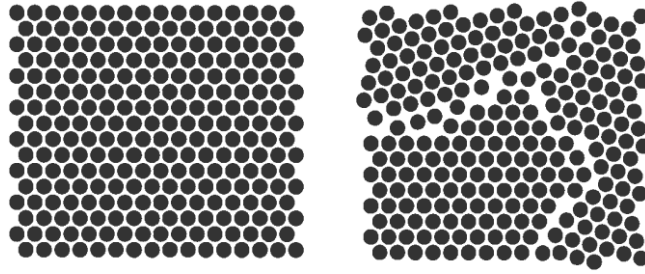If the doping atoms have a valence of three (such as Al), then an unpaired valence electron of one of the surrounding Si atoms can form a state capable of taking an electron, called **acceptor level.**
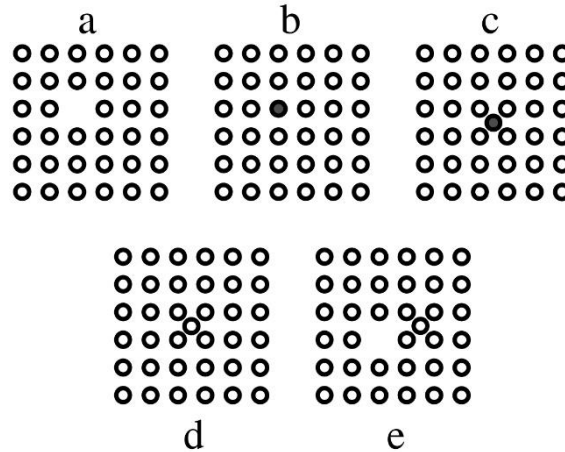
Band structure of doped semiconductors.
Black dots are electrons, white dots are electron vacancies, i.e. holes. The thin dashed line denotes the multitude of donor and acceptor levels.

Lattice Defects

Perfect crystal and lattice defects along granular borders

Point defects:
a) empty vertex, *vacancy* or *Schottky-defect*
b) foreign particle in the lattice (at a vertex), *doping*
c) foreign particle in the interstitial space,
d) lattice particle in the interstitial space (*interstitia*)
a) and d) together, *Frenkel-defect*

From the law of Boltzmann distribution we also expect that perfect crystal structures could only be formed at zero temperature (0 K).

Liquids
Liquid states are governed by **short-range order** (with a range of a few to few hundred times the binding distance).
Liquids are thus **isotropic**, i.e. they have no directional dependence.

Water, surface tension, drops