Institutt for materialteknologi
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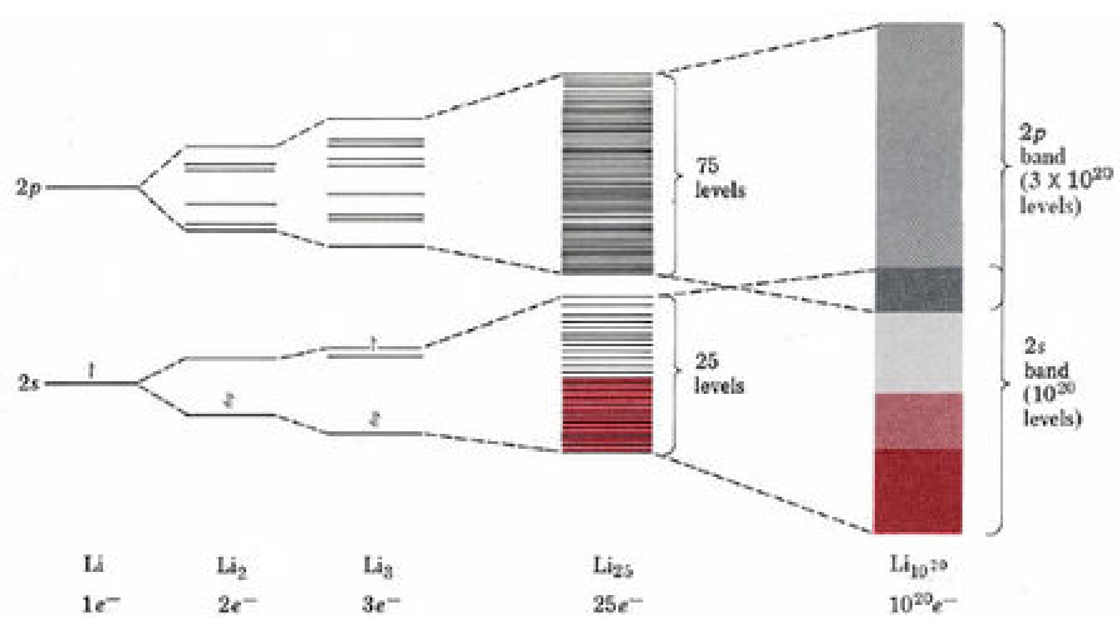
TMT 4320 Nanomaterials, Fall 2015

Solution to exercise 3

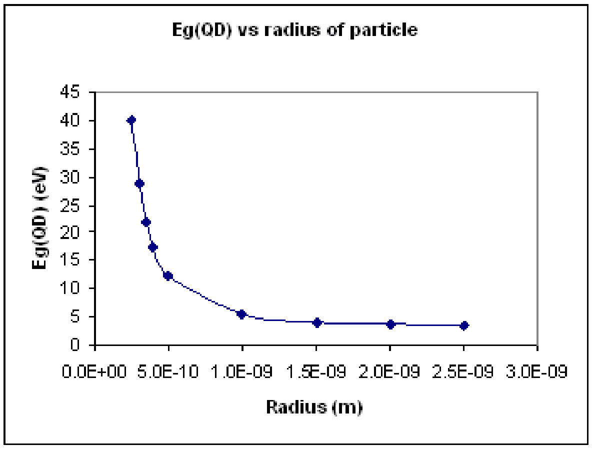
PROPBLEM 1

a) For nanoparticles below a certain size the properties can no longer be defined in terms of bulk properties. There are several factors that may influence this development. First of all, the particle (if crystalline) will start to change its lattice parameter, which in turn changes the electron density of the material. Also, as the particle becomes smaller and smaller, surface effects will become more important since the surface to volume ratio increases dramatically. The morphology and crystal structure of the material may also change. In addition, the continuous energy bands of the bulk collapse into discrete quantized energy levels. This phenomenon is known as the quantum-size effect, and it plays a very important role in QDs. This is illustrated in the figure below which shows the development of an energy band from delocalized molecular orbitals for Li. An isolated atom has sharp energy levels. As the number of atoms increases, the number of discrete orbitals merges into a band of closely spaces energy levels. This figure also illustrates how a metal particle can become semiconducting when the particle reaches a critical size corresponding to a critical number of atoms in the particle.



b)

E_{g0} (eV)	3.2
$\hbar$ (J·s)	1.05E-34
m_e (kg)	1.73E-31
m_h (kg)	1.10E-30
m (kg)	9.11E-31
m_{eh} (kg)	1.50E-31
1 eV =	1.60E-19 J



Diameter (m)	Radius (m)	Eg(QD) (eV)
5.00E-09	2.50E-09	3.566
4.00E-09	2.00E-09	3.772
3.00E-09	1.50E-09	4.218
2.00E-09	1.00E-09	5.490
1.00E-09	5.00E-10	12.359
8.00E-10	4.00E-10	17.511
7.00E-10	3.50E-10	21.892
6.00E-10	3.00E-10	28.642
5.00E-10	2.50E-10	39.837

c) Based on the graph in the previous problem it can be concluded that the critical radius for which quantum size effects start to appear is somewhere between 1.5 and 1.0 nm. There is a slight change in the bandgap even before this point, but the more dramatic increase doesn't start to occur until you get close to a radius of ~1 nm.

PROBLEM 2

Zeolites are crystalline products. The atoms making up the inorganic structure are perfectly ordered and form rows and planes defining a pattern built up from the unit cell which is repeated in all three space directions and satisfies specific rules of symmetry. Crystalline solids have the particularity of producing a well-defined diffraction pattern when illuminated by an X-ray beam, comprising a series of peaks and troughs that provide a sort of identity card for the given material.

The aluminium atoms do not exactly balance the negative charge carried by the oxygen atoms around them. The inorganic structure (framework or skeleton) of the zeolites is thus negatively charged and electrical neutrality of the structure as a whole is achieved by the presence of water molecules and alkali cations, e.g., sodium, potassium, or alkaline earth cations, e.g., calcium, magnesium, occluded within the structure.

The structure comprises an inorganic framework (Si–O–Al) which is an assembly of tetrahedra TO_4 (T = Si, Al). The vertices are occupied by oxygen atoms, and each oxygen atom is shared by two tetrahedra. The molecular dimension channels and cavities that are connected with the surrounding medium vary from 0.3 to 0.8 nm in size. General chemical formula for a zeolite is

$$M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$$

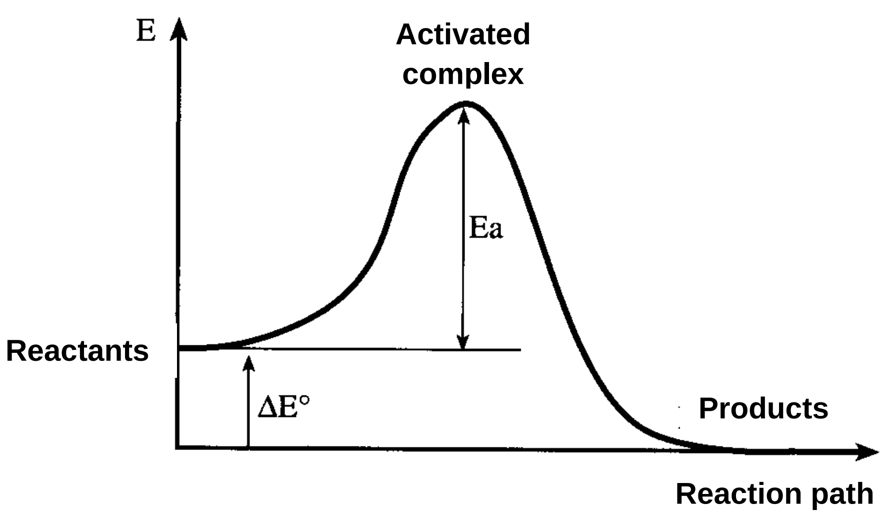
where M is one or more cations of valence *n* and *x* is a number greater than or equal to 2.

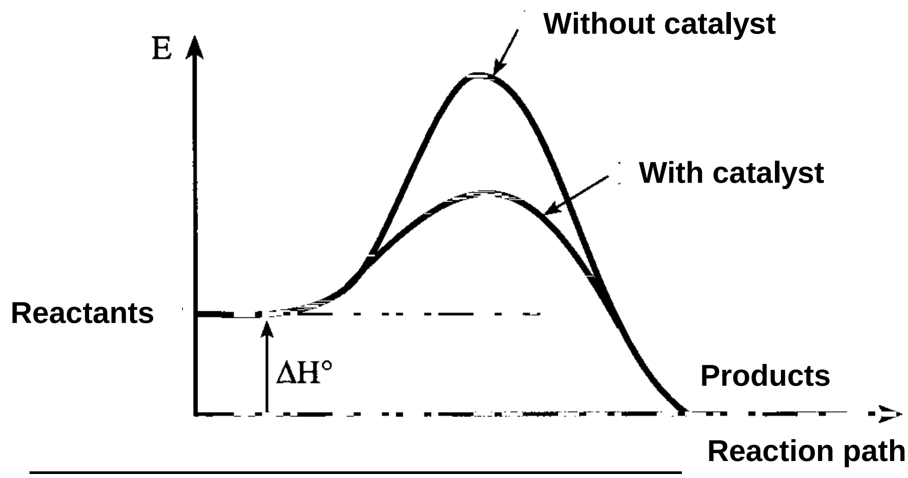
Some application areas for zeolites include fertilizers, molecular sieves, adsorption–drying agents, catalysts, and detergents.

PROBLEM 3

a) What is the difference between homogeneous and heterogeneous catalysis. Homogeneous catalysis is a sequence of reactions that involve a catalyst in the same phase as the reactants. Most commonly, a homogeneous catalyst is codissolved in a solvent with the reactants.

b) The catalyst will decrease the activation barrier for the reaction to take place. This is illustrated in the diagrams on below, where the first diagram shows a reaction with no catalyst present which has a certain activation energy E_a. The second diagram shows the same reaction with the catalyst present, where the activation energy has been lowered about 50%.





c) The main requirement for a reaction to take place is that the total energy of the products must be lower than that of the reactants. If this is not the case, the products will not be stable.