ADVANCED CHEMISTRY BLOC

Story of Scrooge McDuck & Polymorphism

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Scrooge McDuck once purchased a coal mine paying a hefty price. His grandnephews Huey, Dewey and Louie opposed the investment. An adventurer, explorer and businessman Scrooge did not pay any heed to the kids' remark. Surprisingly, uncle Scrooge sowed seeds of peanuts on the land. This made the kids even more mocking. "Uncle, you could have purchased an agricultural land instead for this purpose, why such a costly coal mine" said the kids. As usual, Scrooge gave a stylish laugh and showed confidence in his decision. The plants grew and matured. Elephants from the nearby forest approached in herd and started digging the roots of small plants to find the peanuts. The kids rushed to uncle to inform him about the matter. A smiling Scrooge, rather laughing Scrooge did not pay any attention again. After demolishing the peanut plants the animals went back. Pieces of diamonds appeared in the land.

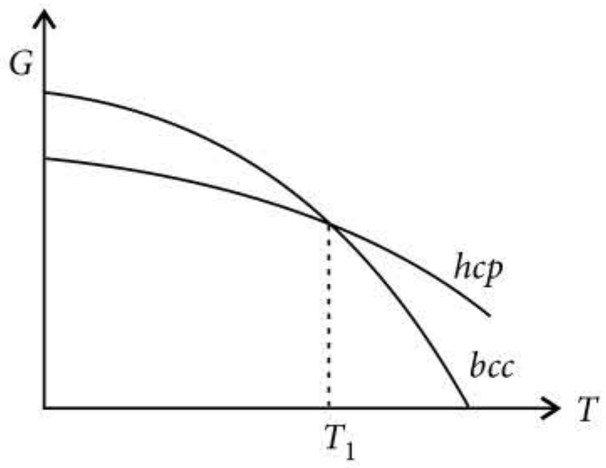
- This famous Walt Disney's cartoon teaches the pressure dependent polymorphism observed in coal in this hilarious way. Though the theme is overstated but it presents polymorphism in a way, which you probably will never forget. The fact is coals cannot be converted to diamonds even under pressure artificially, though graphite can be. Coal contains various impurities; diamond, on the other hand, is the pure form of elemental carbon. The lowest pressure you would need to have would be about 10 GPa and temperature about 4000 K. That's almost a hundred thousand times the normal atmospheric pressure, at a temperature at which basically everything melts.
- It is natural for pressure to induce polymorphic phase changes.
- Temperature dependent polymorphism is common. Many metals and some non-metals may have different types of crystal structures in the solid state depending on temperature. Such crystals are also called allotropic modifications and are usually designated as α, β and γ etc.

The stability of allotropic modifications at definite temperature and pressure is determined by the thermodynamic potential.

$G = H - TS$

The modification having a lower algebraic value of thermodynamic potential at a given temperature is more stable. This lowering of potential can be achieved by lowering enthalpy or raising entropy.

In metallic crystal, the close packed structures are *hcp* and *fcc* (or *ccp*). These two modifications have coordination number 12 and lower enthalpy value. They are stable at lower temperature. The looser *bcc*, with coordination number 8 has higher entropy. As you can see from the graph, beyond temperature T_1, *bcc* structure with lower G is favoured. This explains stability of *bcc* structures in many metals like Ti, Zr, Fe , U at elevated temperature.



Around 30 metals, show temperature dependent polymorphism. Iron is a unique element. It has a *bcc* modification (alpha iron) in lower temperature range, below 912 °C. Then it changes to *ccp* (gamma iron) and then finally *bcc* (delta iron) again at high temperature before it melts to liquid. The low temperature *bcc* in case of iron is because of reasons, which are beyond the scope of this discussion.

- When CsCl (coordination number = 8) is sublimed on to a rough surface it crystallises in the rock salt (coordination number = 6) structure.

The stability of allotropic modifications may change due to changes in the type of bond. For example, the tin modification with diamond type lattice, called alpha tin, is stable at low temperature owing to high energy of covalent bond, and therefore, low enthalpy. On heating it changes to beta tin, which has weaker metallic bond.

Some polymorphous transformations occur under the effect of pressure and temperature. Under very high pressure, iron has a low temperature modification with *hcp* lattice. An increase in pressure at low temperature can change the less closely packed modification into close packed structure. As it has been observed for Ge, Si and alpha tin, application of a high pressure can change their covalent crystals with diamond type lattice (coordination number = 4) into metallic crystal with tetragonal body centered lattice (coordination number = 8). NaCl (coordination number = 6)under high pressure changes to CsCl(coordination number = 8)structure.

Calcite is a carbonate mineral and is the most stable polymorph of calcium carbonate. Other polymorphs of calcium carbonate are aragonite and vaterite.

By virtue of non-directive nature of metallic bonds and closed packed structures, metallic crystals are more plastic and less hard than the covalent crystals.

UNSCRAMBLE ME

Unscramble the words given in column I and match them with their explanations in column II.

Column I	Column II
1. SICOSIDME	(a) A non-enzymatic chemical secreted from the leech that prevents blood clotting.
2. GSNIINRTE	(b) This diagram is often used to grab quickly an idea of which species predominates at specific pH and oxidation-reduction conditions.
3. IDATOCAU	(c) The process by which a particle or a set of particles crosses a barrier on its potential energy surface without having the energy required to surmount this barrier.
4. YPRENOH	(d) A reaction (actual or hypothetical) in which the types of bonds which are made in forming the products are the same as those which are broken in the reactants.
5. DUNIRIH	(e) A biological substance secreted by various cells whose physiological activity is restricted to the vicinity of its release. It is often referred to as local hormone.
6. NGNENILUT	(f) Generic term for Fe(III) complexing compounds released into the medium by bacteria for the purpose of scavenging iron.
7. AIXORUPB	(g) Any process by which the normal alternating donor and acceptor reactivity pattern of a chain, which is due to the presence of O or N heteroatoms, is interchanged.
8. NPOORIC	(h) It refers to the elementary particle present in cosmic radiations. Mass of it is 2185 times that of an electron.
9. NPOULGMU	(i) It refers to a process of bonding by atomic or molecular diffusion wherein powders are heated under pressure but at a temperature below the melting point.
10. DREOERHPOIS	(j) These dyes are a type of azo dyestuffs which can form covalent bonds to cellulose by reactive groups.

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