

“The first crystal analysis proved that in the typical inorganic salt, NaCl, there is no molecular grouping. The inference that the structure consists of alternate ions of sodium and chlorine was an obvious one to make.”

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Solids / Crystal Structure and Solutions

There are four types of solids: (1) *molecular solids* [formed from molecules] (2) *covalent network solids* [formed from atoms] (3) *ionic solids* [formed from ions] and (4) *metallic solids* [formed from metal atoms]. Their physical properties relate closely to the intermolecular and intramolecular forces between the particles.

Types of Solids				
Type of Solid	Form of Unit Partides	Forces Between Partides	Properties	Examples
Molecular	Atoms or molecules	London dispersion, dipole-dipole forces, hydrogen bonds	Fairly soft, low to moderately high melting point, poor thermal and electrical conduction	Argon, Ar; methane, CH ₄ ; sucrose, C ₁₂ H ₂₂ O ₁₁ ; Dry Ice, CO ₂
Covalent-network	Atoms connected in a network of covalent bonds	Covalent bonds	Very hard, very high melting point, often poor thermal and electrical conduction	Diamond, C; quartz, SiO ₂
Ionic	Positive and negative ions electrical conduction	Electrostatic attractions	Hard and brittle, high melting point, poor thermal and electrical conduction	Typical salts—for example, NaCl, Ca(NO ₃) ₂
Metallic	Atoms	Metallic bonds	Soft to very hard, low to very high melting point, excellent thermal and electrical conduction, malleable and ductile	All metallic elements—for example, Cu, Fe, Al, W

Crystalline solids are arranged in fixed geometric patterns or lattices. Examples of crystalline solids are ice and sodium chloride. They have an ordered arrangement of units maximizing the space they occupy, and are practically incompressible. Ionic and atomic crystals are hard and brittle with high melting points. Molecular crystals are soft and have low melting points.

Metallic crystals are composed of positively charged ions in a field of freely moving electrons. Amorphous solids have a random orientation of particles. Examples of amorphous solids are glass and plastic. They are considered super-cooled liquids in which the molecules are arranged in a random manner similar to the liquid state. More than 90% of naturally occurring and artificially prepared solids are crystalline. Minerals, sand, clay, limestone, metals, alloys, carbon (diamond and graphite), salts (NaCl, KCl etc.) , all have crystalline structures.

Crystalline structure is formed by repeating a three dimensional pattern of atoms, ions or molecules. Repetition of the structural units of the substance over long atomic distances is referred to as *long-range order*. Liquids and amorphous solids (e. g. glass) do not have *long-range order*, but have a limited, localized order proximate to their structural units.

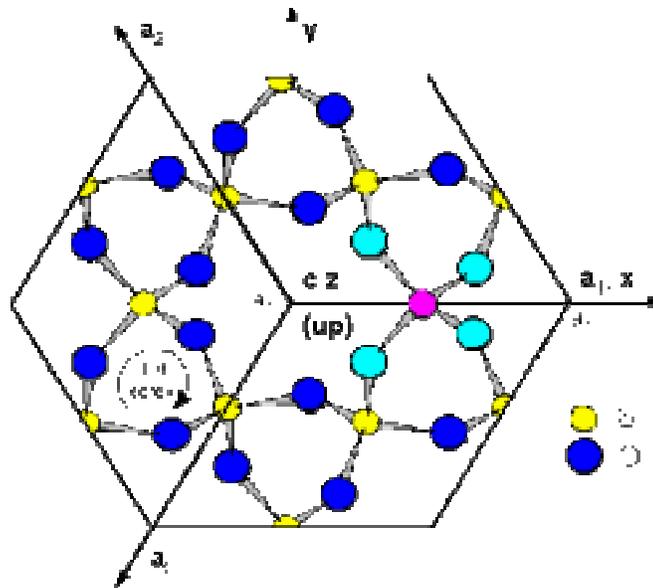
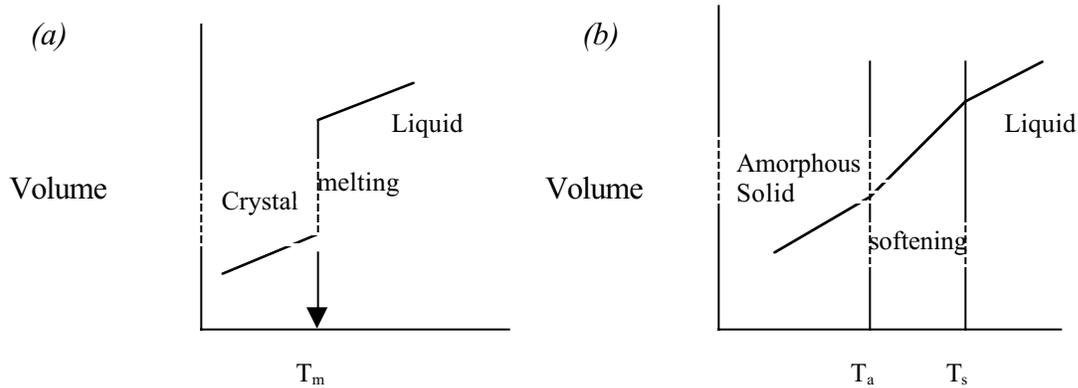


Fig.1 Schematic structure of SiO₂: crystalline quartz, including orientation along the x, y and z axes

The physical properties of liquids and amorphous solids are identical in all directions along any axis. These are referred to as *isotropic properties*. Optical, electrical and mechanical properties of crystals relate to orientation and are dependent on the crystal's axes. These are referred to as *anisotropic properties*. It is the reason for using selected parts of a crystal for different devices having unique properties (eg. Segnetoelectrics and piezoelectrics).

A second difference between solids in a crystalline versus amorphous state is their behavior when they are heated. Crystals become liquids at a specific temperature, T_m (the melting point). At this temperature physical properties of the crystalline solids change sharply. Amorphous solids soften gradually when they are heated. There tends to be a relatively wide temperature range for the melting point, a zone between the solid and the liquid state where physical properties of the substance change gradually.



*Fig.2 Volume vs. Temperature
Heating a crystalline solid (a) and an amorphous solid (b)*

The crystalline state is relatively more stable state than the amorphous state. So, the Gibbs Free Energy, ΔG , of a substance in the amorphous state is always higher than the Gibbs Free Energy of that same substance in its crystalline state. This accounts for the transformation of an amorphous solid into its crystalline state. The reverse, transformation from the crystalline state to the amorphous state, does not occur because it is energetically unfavored ($\Delta G > 0$). However, the energy difference between the amorphous and crystalline state is relatively small, so the amorphous solid is quite stable.

Transformation of amorphous substances into crystalline solids is rarely observed. This is attributed to the high viscosity of solids, which allows change to occur, but only very slowly. The colossal viscosity of silicate glasses can preserve them for thousands of years without any indication of crystallization.

Usually, crystalline solids are aggregates consisting of many small crystals providing an irregular shape to a large crystal mass. However, single crystals do occur in nature, and they can be grown artificially for a number of important applications.

Crystallization is the process of forming and growing crystals from melted solids, solutions and vapors. Crystals can form due to supersaturation or super-cooling. Crystallization may take more or less time: structural units need time to build up a crystalline order. The higher symmetry of structural units and the weaker the forces that are between them, the more likely and more rapidly crystallization occurs. Melted metals crystallize very easily. Melted silicates undergo transfer into an amorphous state while cooling.

Only linear, stereo-regular and very elastic macromolecules are able to crystallize. Due to their dimensions and strong intermolecular forces, the crystallization process is very slow, and complete crystallization usually does not occur. Besides a crystalline phase there also can be an amorphous phase in synthetic polymers.

Unit Cells

- *Crystalline solid*: is a well-ordered, definite arrangements of molecules, atoms or ions.
- *Crystals* have an ordered structure, which repeats itself.
- The smallest repeating unit in a crystal is a *unit cell*.
- The unit cell is the smallest unit. It has the same *symmetry* as the entire crystal.
- Three-dimensional packing of unit cells produces the *crystal lattice*.
- There are seven different unit cells:

Cubic: All three axes have same length and intercept at right angles. Typical crystal shapes are the cube, octahedron, rhombic dodecahedron, icosi-tetrahedron, and hexacisochedron.

Tetragonal: The three axes intercept at right angles, but one axis is longer or shorter than the other two equal axes. Typical crystal shapes are four-sided prisms and pyramids, trapezohedrons and eight-sided pyramids, and double pyramids.

Hexagonal: Three of the four axes are in one plane, intercept at 120° , and are of the same length. The main axis is longer or shorter and is normal to the plane of the other three. Typical crystal shapes are hexagonal prisms and pyramids and twelve-sided pyramids and double pyramids.

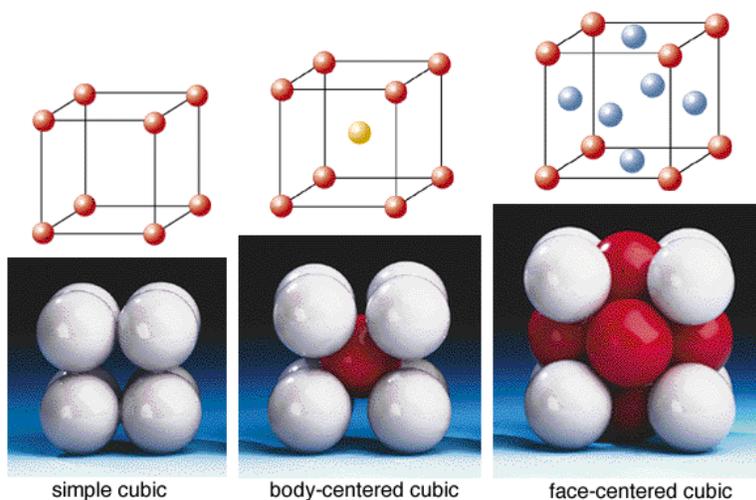
Trigonal (rhombohedral): Same axes as hexagonal, but having a cross section showing three-sided symmetry instead of six-sided. Typical crystal shapes are three-sided prisms and pyramids, rhombohedra, and scalenohedra.

Orthorhombic: The three axes are of different lengths and are at right angles to each other. Typical crystal shapes are basal pinacoids, rhombic prisms and pyramids, and rhombic double pyramids.

Monoclinic: The three axes are of different lengths and two are at right angles to each other. The third axis is included. Typical crystal shapes are basal pinacoids and prisms with included end faces.

Triclinic: All three axes are of different lengths and form oblique angles. Typical crystal shapes are paired faces.

Three common cubic examples:



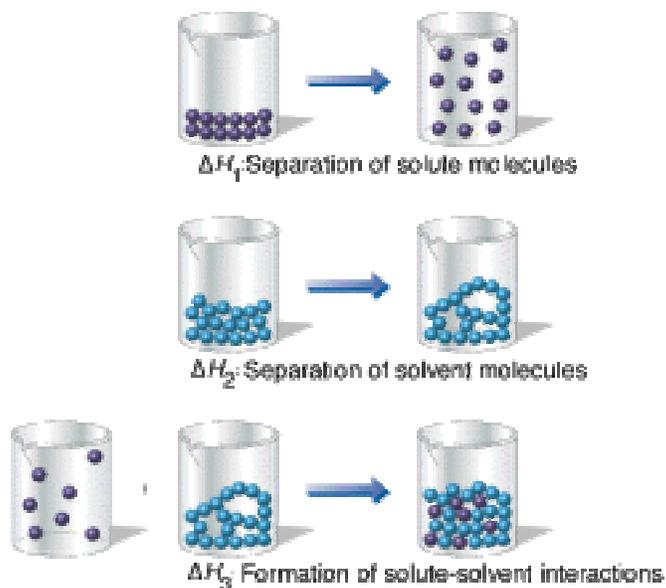
Energy and Solution Formation

Two energy changes contribute to the formation of a solution—or the lack thereof. The sum of the effects of the change in the heat content of the system (enthalpy, ΔH) minus the change in the disorder of the system (entropy, ΔS). The result must provide an overall release of energy ($\Delta G < 0$) to do work if a solution is to form. Let's consider each of these processes separately.

Although the process of solution formation is dynamic, the related energies are state functions. Each can be broken down into distinct energetic steps. The energy associated with each step can be used in a Hess's Law type of calculation to obtain the net energy released or absorbed.

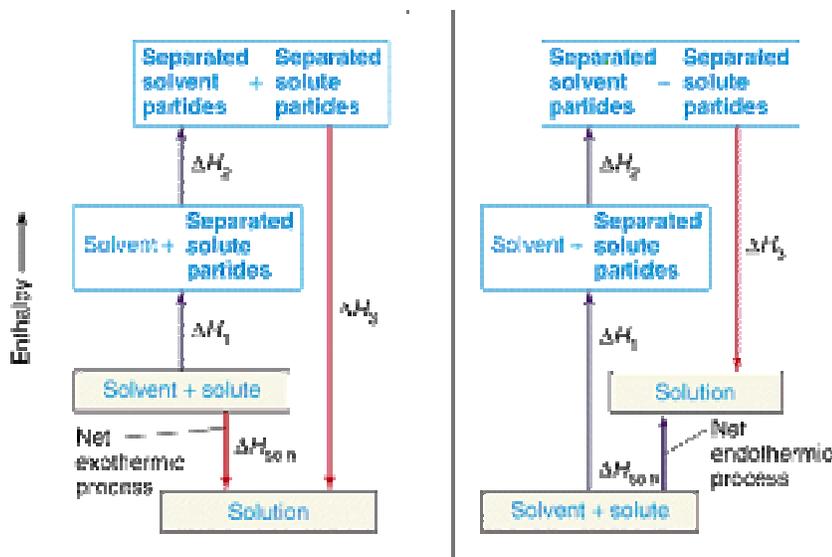
$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

On a molecular level the steps in the formation of a solution can be broken down into the following interactions: (a) among the solute particles, ΔH_1 , (b) among the solvent particles, ΔH_2 , and (c) between the solute and solvent particles, ΔH_3 . Breaking attractive intermolecular forces is always endothermic ($\Delta H_1 > 0$ and $\Delta H_2 > 0$). Forming attractive intermolecular forces is always exothermic ($\Delta H_3 < 0$).



If table salt, sodium chloride, dissolves in water: NaCl is the solute and water is the solvent. Water's hydrogen bonds break; NaCl_(s) dissociates into Na⁺_(aq) and Cl⁻_(aq); ion-dipole forces form: Na⁺ ⋯ δ⁻OH₂ and Cl⁻ ⋯ δ⁺H₂O. The ions are *solvated* by water; more specifically they are *hydrated*.

Consider the following energy diagrams, does NaCl follow the diagram on the left or the right?
Hint: Does the glass get warmer or colder?



The other process to consider in analyzing solution formation is the natural tendency toward increasing disorder. In most cases, when solutions form, there is an increase in disorder ($\Delta S > 0$) that results from mixing the solute and solvent. This is an energetically favorable process.

As mentioned earlier, the overall process must release Free Energy ($\Delta G < 0$). This is determined by the following relationship to enthalpy and entropy.

$$\Delta G = \Delta H - T\Delta S$$

Name(s): _____

<i>Workshop: Solids / Crystals</i>

1. Distinguish between a crystalline solid and an amorphous solid.
2. Compare and contrast crystalline and amorphous solids in terms of their particulate and macroscopic characteristics. Give examples of each.
3. If a bag of 100 marbles was emptied into a box, would the arrangement of the marbles most resemble a crystalline or an amorphous solid at the particulate level? Explain. How could you rearrange the marbles to have the opposite arrangement?
4. Why it is possible to produce sheets and wire from metals, and it is not possible to produce to produce sheets and wire from ionic salts, e.g. NaCl?
5. Draw a two dimensional scheme of a structure of a metal crystal and of an ionic crystal (NaCl). Explain what will happen when a mechanical stress is applied in the x-direction.

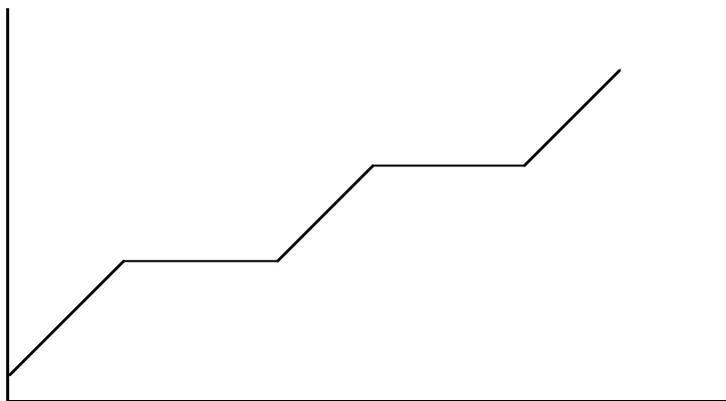
Name(s): _____

Workshop: Phases/Forces

1. Compare and contrast the distances between particles in the solid, liquid, and gaseous states. How do the distances relate to the relative intermolecular attractive forces?
2. List the three major intermolecular forces in order of increasing strength.
3. How do intermolecular forces affect the physical properties of a compound?
4. Define and compare heat (enthalpy) of vaporization and heat (enthalpy) of fusion.
5. What are the similarities and differences between *intermolecular* forces and *intramolecular* forces (chemical bonds)? Brainstorm to come up with a list of items that can be used to compare the forces, and then discuss the items on your group's list. Finalize the answer to the question by listing at least two similarities and differences between the types of forces.
6. The term *hydrogen bonding* implies that this phenomenon is a chemical bond, yet it is listed in the "intermolecular forces" section of most textbooks. Is a hydrogen bond a bond or not? Explain.

7. What characteristics must be present in a molecule in order for hydrogen bonding to occur? Give three examples of molecules that will exhibit hydrogen bonding and three examples of molecules that will *not* exhibit hydrogen bonding *even though they have hydrogen atoms*.
8. How can a nonpolar molecule—one with a symmetric distribution of electronic charge—become a dipole? Discuss the answer to this question with your group, and then write a one paragraph summary of your answer.
9. How do you identify nonpolar molecules? Can a molecule made from different elements, such as CH_4 , be nonpolar? Are all molecules made from the same element, such as H_2 , nonpolar? Explain.
6. A glass is partially filled with ice and then liquid water is added. The contents are stirred occasionally over a period of ten minutes, after which both ice and liquid water are in the glass. What is the temperature of the ice water? How do you know the answer to this question.
7. What will the temperature be after another ice cube is added to the mixture?

8. Consider the following plot of temperature versus energy for a pure substance.



Which variable is plotted on which axis?

What state(s) of matter exist(s) in each of the five sections of the curve?

Explain why the two horizontal sections of the curve exist, in terms of particulate behavior.

