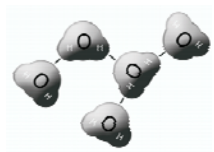
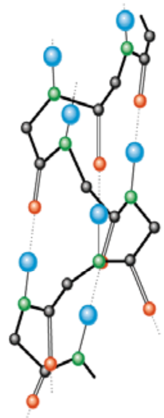
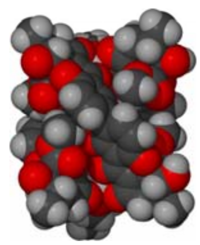


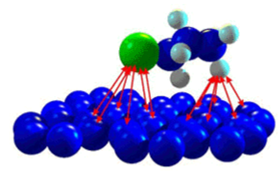
Chapter 12

Intermolecular Forces and Physical Properties of

Liquids and Solids







Types of Crystals

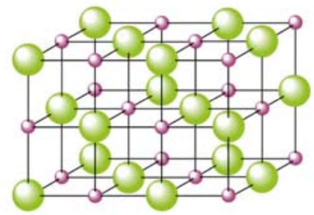
- There are four main types of crystalline solids:
  - Ionic crystals.
  - Covalent crystals.
  - Molecular crystals.
  - Metallic crystals.

- These crystals have different kinds of forces and properties.

Chapter 12 Section 4

Ionic Crystals

- Lattice points occupied by charged spheres (cations and anions) held together by columbic forces.
- Size and relative number of each ion determine the crystal structure.
- Anions generally are bigger than cations. Thus, in many cases we use anions to identify the unit cell of a given lattice structure.



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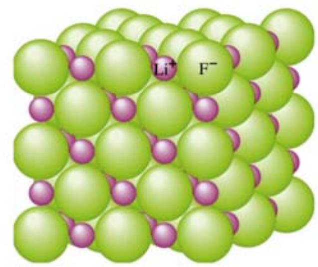

(b)

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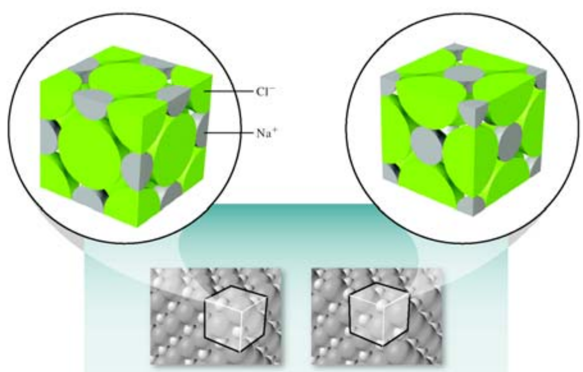
Ionic Crystals

What type of unit cells do Cl^- and Na^+ ions adopt?

Faced-centered cubic unit cell (*fcc*).

How many Cl^- and Na^+ spheres are there in each unit cell?

Four spheres each.



The unit cell of an ionic compound always contains the same ratio of cations to anions in the formula unit. → **NaCl**

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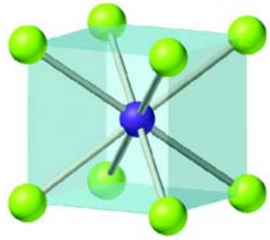
Other Examples of Ionic Crystals

What type of unit cells does Cl^- ions adopt?

simple cubic unit cell (*scc*).

How many Cl^- and Cs^+ spheres are there in each simple cubic unit cell?

one sphere each.



CsCl

The unit cell of an ionic compound always contains the same ratio of cations to anions in the formula unit.

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Other Examples of Ionic Crystals

What type of unit cells do S^- ions adopt?

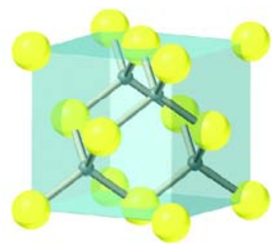
Faced-centered cubic unit cell (*fcc*).

How many S^- and Zn^+ spheres are there in each *fcc* unit cell?

Four sphere each.

ZnS has the ***zincblende*** structure which is based on the *fcc* lattice. Zn^+ are arranged tetrahedrally about each S^- ions.

Other example of ionic compounds that adopt the zincblende structure are CuCl, BeS and CdS.



ZnS

The unit cell of an ionic compound always contains the same ratio of cations to anions in the formula unit.

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Chapter 12 Section 4

Other Examples of Ionic Crystals

What type of unit cells do Ca^{2+} ions adopt?

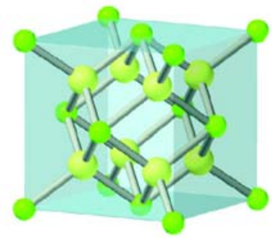
Faced-centered cubic unit cell (*fcc*).

How many Ca^{2+} and F^- spheres are there in each *fcc* unit cell?

Four Ca^{2+} spheres and eight F^- spheres.

CaF_2 has the ***fluorite*** structure which is also based on the *fcc* lattice.

Other example of ionic compounds that adopt the fluorite structure are SrF_2, $BaCl_2$ and PbF_2.



CaF_2

Here, the Ca^{2+} ions occupy the lattice points, and each F^- ion is surrounded tetrahedrally by four Ca^{2+} ions.

The unit cell of an ionic compound always contains the same ratio of cations to anions in the formula unit.

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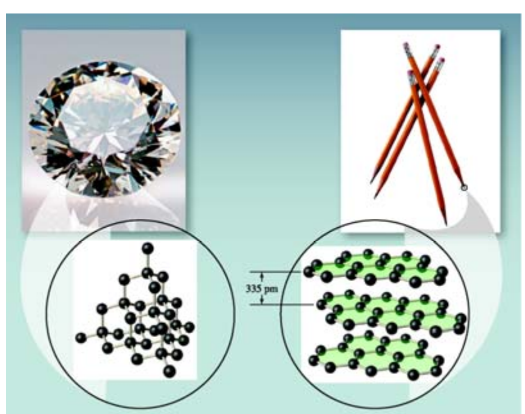
Covalent Crystals

- Atoms are held together by covalent bonds.



diamond graphite

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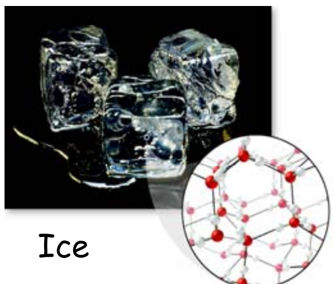
Chapter 12 Section 4

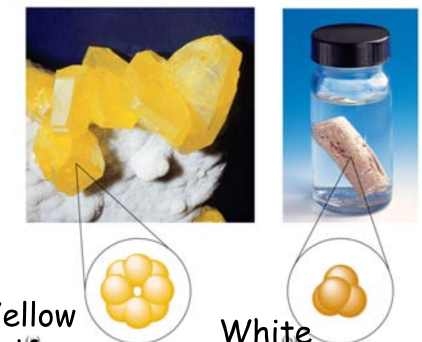
Molecular Crystals

- Lattice points occupied by molecules (or atoms).
- Held together by intermolecular forces (dipole-dipole, hydrogen bonding, dispersion forces).



Ice

What kind of forces are there in ice and sulfur?



Yellow sulfur

White sulfur

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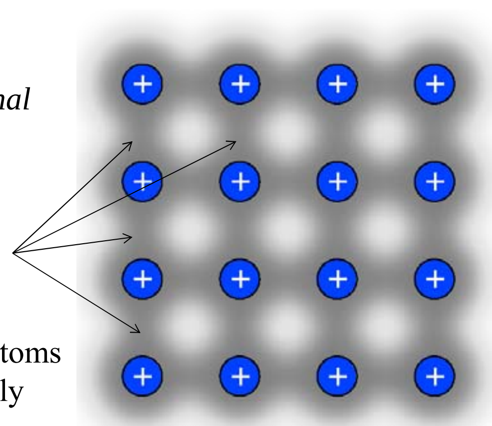
Chapter 12 Section 4

Metallic Crystals

- Lattice points occupied by atoms.
- Generally *bcc*, *fcc*, *hexagonal* closest packed.
- Very dense.
- Strong bonding arises from ***delocalized electrons***.
- ***Electron sea model:*** It is difficult to separate metal atoms (hardness), but it is relatively easy to move them around (ductility and malleability).



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Chapter 12 Section 4

Types of Crystals

TABLE 12.4 Types of Crystals and Their General Properties

Type of Crystal	Cohesive Forces	General Properties	Examples
Ionic	Coulombic attraction and dispersion forces	Hard, brittle, high melting point, poor conductor of heat and electricity	NaCl, LiF, MgO, $CaCO_3$
Covalent	Covalent bonds	Hard, brittle, high melting point, poor conductor of heat and electricity	C (diamond),* SiO_2 (quartz)
Molecular†	Dispersion and dipole-dipole forces, hydrogen bonds	Soft, low melting point, poor conductor of heat and electricity	Ar, CO_2, I_2, H_2O, $C_{12}H_{22}O_{11}$
Metallic	Metallic bonds	Variable hardness and melting point, good conductor of heat and electricity	All metallic elements, such as Na, Mg, Fe, Cu

*Diamond is a good conductor of heat.

†Included in this category are crystals made up of individual atoms.

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Exercise

The radius of a gold atom is 144 pm. The density of gold is 19.32 g/cm^3 and its molar mass is 197.0 g/mol. Does gold have an *fcc* structure or a *bcc* structure?

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Chapter 12 Section 5

Amorphous Solids

- They lack regular arrangement of atoms. Examples are charcoal, powder and glass.
- Glass is a familiar and important amorphous solid.
  - Transparent fusion of inorganic materials (mainly SiO_2) that have been cooled without crystallizing.
  - Behaves more as a liquid than a solid

TABLE 12.5 Composition and Properties of Three Types of Glass

Pure quartz glass	100% SiO_2	Low thermal expansion, transparent to a wide range of wavelengths. Used in optical research.
Pyrex glass	60%–80% SiO_2, 10%–25% B_2O_3, some Al_2O_3	Low thermal expansion; transparent to visible and infrared, but not to ultraviolet light. Used in cookware and laboratory glassware.
Soda-lime glass	75% SiO_2, 15% Na_2O, 10% CaO	Easily attacked by chemicals and sensitive to thermal shocks. Transmits visible light but absorbs ultraviolet light. Used in windows and bottles.

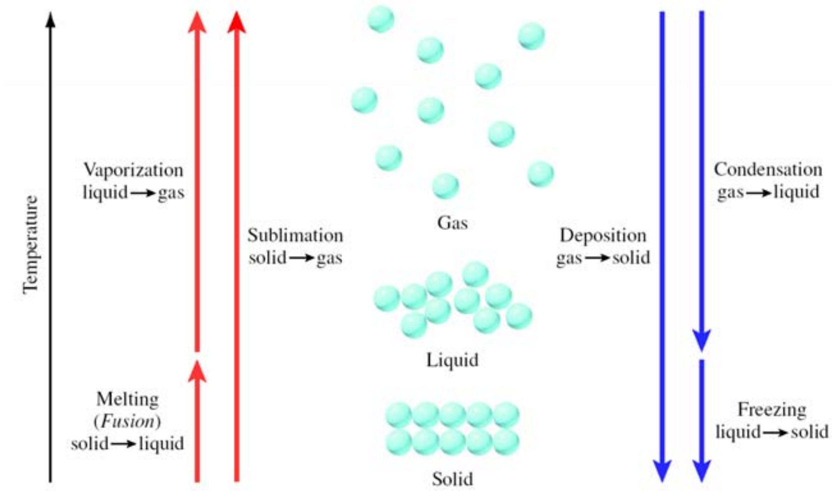
Chapter 12 Section 6

Phase Changes

- ***Phase*** – a homogenous part of a system that is separated from the rest of the system by a well-defined boundary.
- ***Phase change*** – transition from one phase to another.
  - Caused by the removal or addition of energy.
  - Energy involved is usually in the form of heat.

Chapter 12 Section 6

The Six Possible Phase Changes



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Chapter 12 Section 6

Liquid-Vapor Phase Transition

- Vapor pressure of a liquid increases with temperature.

  When the vapor pressure reaches the external pressure, *the liquid boils*.
- ***Boiling point*** – the temperature at which the vapor pressure of liquid equals the atmospheric pressure.

  The boiling temperature varies with the external pressure.

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Liquid-Vapor Phase Transition

- ***Molar heat of vaporization* (ΔH_{vap})** : it is the amount of heat required to vaporize one mole of a substance at its boiling point. It is usually expressed in kJ/mol.
- ΔH_{vap} is dependent on the strength of intermolecular forces.

TABLE 12.6 Molar Heats of Vaporization for Selected Liquids

Substance	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
Argon (Ar)	−186	6.3
Benzene (C_6H_6)	80.1	31.0
Ethanol (C_2H_5OH)	78.3	39.3
Diethyl ether ($C_2H_5OC_2H_5$)	34.6	26.0
Mercury (Hg)	357	59.0
Methane (CH_4)	−164	9.2
Water (H_2O)	100	40.79

Chapter 12 Section 6

Liquid-Vapor Phase Transition

- ***Condensation*** : opposite to vaporization.
- The condensation (liquefaction) process can be achieved either by:
  - Cooling the sample.
  - Applying pressure on the sample.
- ***Critical temperature*** (T_c) – the temperature above which a gas cannot be liquefied by applying pressure.
- ***Critical pressure*** (P_c) – the pressure that must be applied to liquefy a gas at T_c.
- ***Supercritical fluid*** – the fluid that exists above T_c and P_c.

Chapter 12 Section 6

Liquid-Vapor Phase Transition

TABLE 12.7 Critical Temperatures and Critical Pressures of Selected Substances

Substance	T_c (°C)	P_c (atm)
Ammonia (NH_3)	132.4	111.5
Argon (Ar)	−122.2	6.3
Benzene (C_6H_6)	288.9	47.9
Carbon dioxide (CO_2)	31.0	73.0
Ethanol (C_2H_5OH)	243	63.0
Diethyl ether ($C_2H_5OC_2H_5$)	192.6	35.6
Mercury (Hg)	1462	1036
Methane (CH_4)	−83.0	45.6
Molecular hydrogen (H_2)	−239.9	12.8
Molecular nitrogen (N_2)	−147.1	33.5
Molecular oxygen (O_2)	−118.8	49.7
Sulfur hexafluoride (SF_6)	45.5	37.6
Water (H_2O)	374.4	219.5

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Chapter 12 Section 6

Solid-Liquid Phase Transition

- ***Freezing*** – transformation of liquid to solid.
- ***Melting*** (***fusion***) : opposite to freezing.
- ***Melting point*** of solid (or ***freezing point*** of liquid) is the temperature at which the solid and liquid phases coexist in equilibrium.
  - Dynamic equilibrium in which the forward and reverse processes are occurring at the same rate.

    At 0˚C and 1 atm, the dynamic equilibrium for H_2O is represented by:

$$\text{ice} \leftrightarrow \text{water}$$

$$H_2O(s) \leftrightarrow H_2O(l)$$

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Solid-Liquid Phase Transition

- ***Molar heat of fusion*** **(ΔH_{fus})** : it is the amount of heat required to melt one mole of a solid. It is usually expressed in kJ/mol.

Which one do you think is greater for H_2O;
ΔH_{vap} or ΔH_{fus}?

$H_2O(s) \rightarrow H_2O(l) \quad \Delta H^o_{fus} = 6.02$ kJ/mol
$H_2O(l) \rightarrow H_2O(g) \quad \Delta H^o_{vap} = 40.7$ kJ/mol

Chapter 12 Section 6

Solid-Liquid Phase Transition

TABLE 10.9 Melting Points and Enthalpies of Fusion for Several Representative Solids

Compound	Melting Point (°C)	Enthalpy of Fusion (kJ/mol)
O_2	−218	0.45
HCl	−114	1.99
HI	−51	2.87
CCl_4	−23	2.51
$CHCl_3$	−64	9.20
H_2O	0	6.02
NaF	992	29.3
NaCl	801	30.2

Chapter 12 Section 6

Solid-Vapor Phase Transition

- ***Sublimation***: a process in which the substance goes directly from the solid to the gaseous states.

Dry Ice (CO_2)

Iodine (I_2)

Moth Balls

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Solid-Vapor Phase Transition

- ***Molar heat of sublimation*** (ΔH_{sub}) : it is the amount of energy required to sublime one mole of solid usually in kJ/mol.

$$\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$$

- ***Deposition*** – reverse of sublimation

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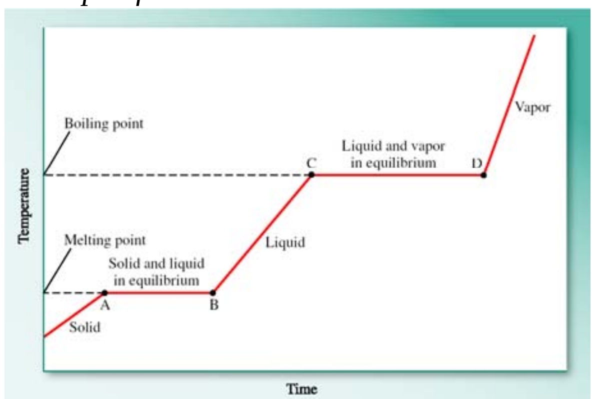
Chapter 12 Section 6

Heating Curve

- The changes in the state of a matter can be represented by a ***heating curve***, which is a plot of temperature vs. time for a process when an energy is added in a *constant rate* to a *specific amount* of a substance.



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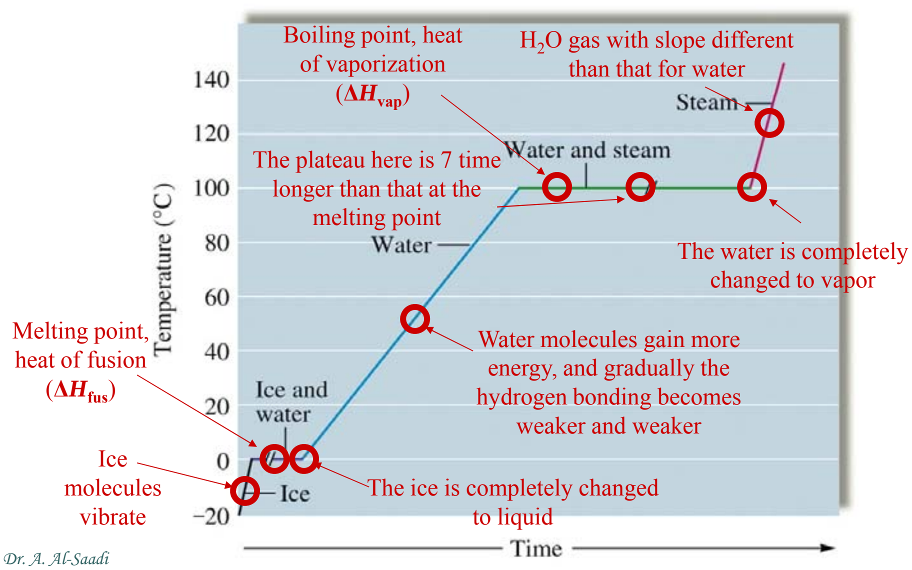
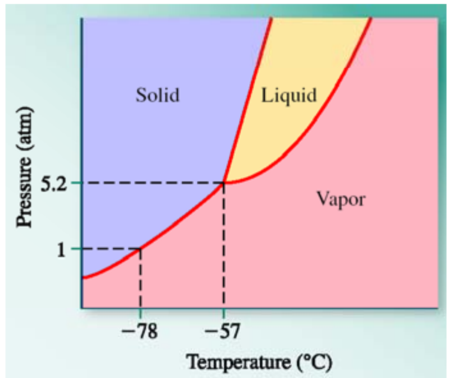
Heating Curve for Water



Phase Diagrams

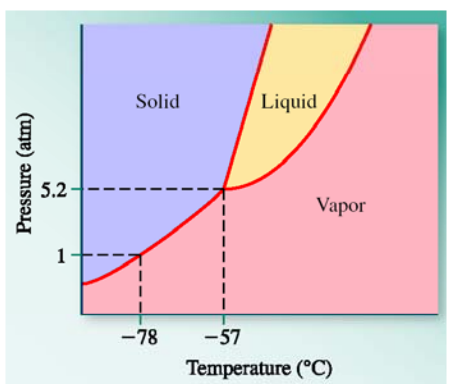
- ***Phase diagram*** – summarizes the conditions (temperature and pressure) at which a substance exists as a solid, liquid or gas
  - Divided into three regions (solid, liquid, vapor).
  - ***Phase boundary line*** – line separating any two regions. It indicates conditions at which two phases can exist in equilibrium.



The phase diagram for CO_2

Phase Diagrams

- ***Phase diagram*** – summarizes the conditions (temperature and pressure) at which a substance exists as a solid, liquid or gas
  - ***Triple point*** – the point at which all three phase boundary lines meet. It indicates the *T* and *P* at which all three phase of a substance exist in equilibrium.

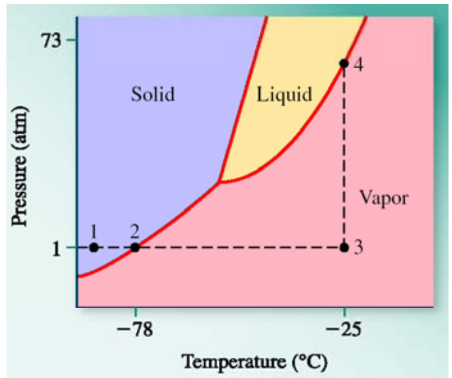


The phase diagram for CO_2

Chapter 12 Section 7

Phase Diagrams of CO_2

- The phase diagram gives a lot of information about the phase transitions under different conditions of pressure and temperature.



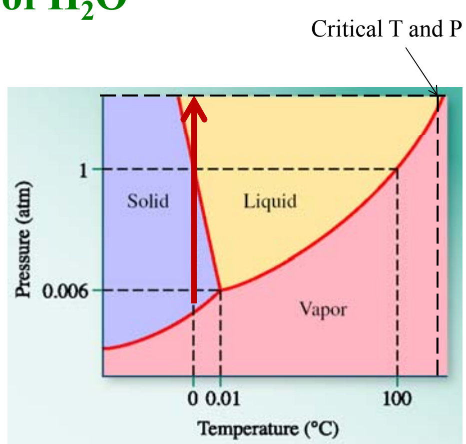
The phase diagram for CO_2

Chapter 12 Section 7

Phase Diagrams of H_2O

- The phase diagram of water is unusual because the solid-liquid phase boundary has a negative slope.

  By applying pressure, H_2O can be liquefied. This is because the *density of ice is less than water* at the melting point.

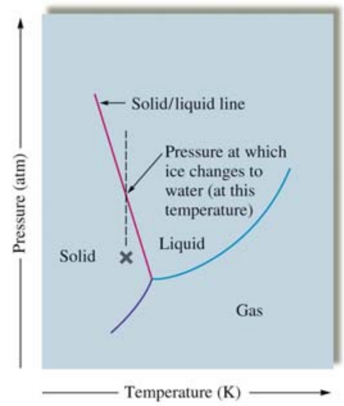


The phase diagram for H_2O

Chapter 12 Section 7

Phase Diagram of H_2O

- Applications of that special physical properties of water:
  - Ice skating (more pressure from the skater's blade causes the ice to convert into water).
  - Pipe freezing causes them to crack.
  - Ice formed on lakes floats.



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Chapter 12 Section 7

Exercises on Phase Diagrams

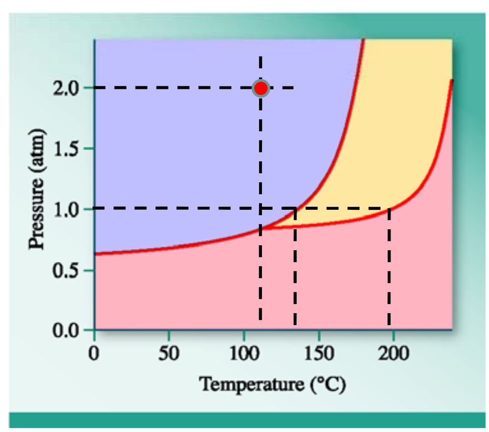
- What is:

  a) the normal* melting point,

  b) the normal* boiling point

  c) the physical state of the substance at 2.0 atm and 110˚C?

*normal – measured at 1.00 atm



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