

Chapter 16

Liquids and Solids

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1

Physical States

Gases

- Low density
- High compressibility
- Completely fill a container

Solids

- Much greater density
- Compressible only to a very slight extent
- Rigid
- Maintains its shape irrespective of its container
- Components close together and exert large attractive forces

Liquids

- Lie somewhere between those of solids and those of gases
- But not midway between

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2

Liquids vs Solids

➤ Compare the enthalpy change for the melting of ice at 0°C (the heat of fusion) with that for vaporizing liquid water at 100°C (the heat of vaporization):

$\text{H}_2\text{O (s)} \rightarrow \text{H}_2\text{O (l)} \quad \Delta H^\circ_{\text{fus}} = 6.02 \text{ KJ/mol}$

$\text{H}_2\text{O (l)} \rightarrow \text{H}_2\text{O (g)} \quad \Delta H^\circ_{\text{vap}} = 40.7 \text{ KJ/mol}$

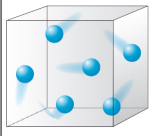
➤ The relative similarity of the liquid and solid states can also be seen when comparing the densities of the three states of water (Table 16.1).

TABLE 16.1	
Densities of the Three States of Water	
State	Density (g/cm ³)
Solid (0°C, 1 atm)	0.9168
Liquid (25°C, 1 atm)	0.9971
Gas (400°C, 1 atm)	3.26×10^{-4}

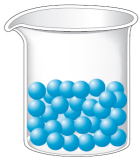
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Liquids vs Solids

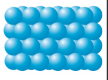
- The liquid and solid states show many similarities and are strikingly different from the gaseous state.



Gas



Liquid



Solid

FIGURE 16.1: Densities of three states of water

Intermolecular Forces

- Intramolecular forces** hold atoms together in a molecule.
- Intermolecular forces (van der Waals forces)** are attractive forces between molecules.
- Intermolecular vs Intramolecular**
 - 41 kJ to vaporize 1 mole of water (inter)
 - 930 kJ to break all O-H bonds in 1 mole of water (intra)

"Measure" of intermolecular force

- Generally, intermolecular forces are much weaker than intramolecular forces.

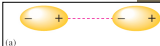
boiling point

melting point

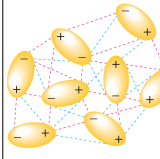
ΔH_{vap} , ΔH_{fus} , ΔH_{sub}

Dipole-Dipole Interactions

- Dipole-dipole interactions** are the forces that exist between polar molecules.
- Polar molecules have opposite end charges (a partial positive side and a partial negative charge).
- When a large number of polar molecules are together, they tend to orient themselves so that the partially positive end of one is near the partially negative end of another.
- The electrostatic attraction of (partial) opposite charges leads to a net attraction between the molecules called **dipole-dipole interaction**.



(a)



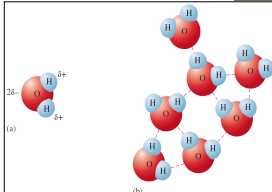
(b)

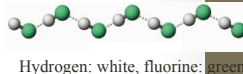
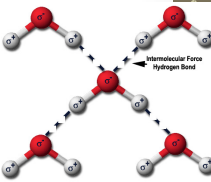
Attraction: - - - - -

Repulsion: - - - - -

Hydrogen-Bonding

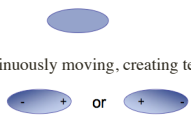
- Strong dipole-dipole forces are seen among molecules in which hydrogen is bound to a highly electronegative atom, such as nitrogen, oxygen, or fluorine.
- Special name associated with this strong intermolecular force: **hydrogen bond**.
- Factors that account for the unusual strength of a hydrogen bond are:
 - The great polarity of the bond.
 - The close approach of the dipoles, allowed by the very small size of the hydrogen atom.



- In HF, hydrogen bonds exist between the highly electronegative F atom of one HF molecule and a hydrogen atom of another HF molecule in a zig-zag arrangement.
 
- Significant amount of energy is required to separate the molecules, which leads to a high boiling point.
- Water molecules also interact with each other *via* hydrogen bonding.
 
- Although F is more electronegative than O, the hydrogen bonds between H₂O molecules are stronger than in HF, since H₂O has two H atoms that can hydrogen bond to other water molecules.

This explains why H₂O has a higher boiling point than HF.

Induced Dipole-Induced Dipole Interactions: London Dispersion Forces

- Even molecules without dipole moments exert forces on each other.
- Non-polar molecules interact with each other *via* **induced dipole-induced dipole forces**. These are also called **London forces and dispersion forces**.
 - These are weaker than dipole-dipole interactions.
- On average, non-polar bonds have an equal distribution of electrons (charge).
- Electrons are continuously moving, creating temporary dipoles.
 

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- A temporary dipole in one molecule can induce a temporary dipole in another molecule

- The synchronized movement of electrons can occur over huge numbers of molecules (as long as they're close together)

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10

London Dispersion Forces


- Non-polar molecules can develop a momentary non symmetrical electron distribution that produces a temporary dipolar arrangement of charge.
- This is an *instantaneous dipole* and can then *induce* a similar dipole in the neighboring atom.
- This phenomenon leads to an interatomic attraction that is both weak and short-lived but that can be very significant for large atoms (noble gases) and molecules.

The Liquid State

- Liquids exhibit many characteristics such as low compressibility, lack of rigidity and high density compared to gases.
- When liquids are poured onto a solid surface, they tend to bead as droplets, a phenomenon that depends on the intermolecular forces.
- Although molecules in the interior are completely surrounded by other molecules, those at the liquid's surface are subject to attractions only from the side and from below (Figure 16.6).


Surface Tension

- Molecules at the surface cohere more strongly to those directly associated with them on the surface. This enhancement of the intermolecular attractive forces at the surface is called **surface tension**.
- Large intermolecular forces tend to lead to relatively high surface tensions.
- The effect of the uneven pull on the surface molecules tends to draw them into the body of the liquid and causes a droplet of liquid to assume the shape that has the minimum surface area – a sphere.
- The resistance of a liquid to an increase in its surface area is called the **surface tension** of the liquid.



Liquid Forces

- Polar liquids also exhibit **capillary action** - the spontaneous rising of a liquid in a narrow tube.
- Two different types of forces are responsible for this:
 1. **Cohesive forces**: Intermolecular forces among the molecules of the liquid
 2. **Adhesive forces**: Forces between the liquid molecules and their container.
- Adhesive forces between a polar liquid and a given surface are strongest when the surface is made of a substance that has polar bonds.
- For example, glass contains many oxygen atoms with partial negative charges that are attracted to the positive end of a polar molecule such as water.




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14

Liquid Forces

- The ability of water to “wet” glass makes it creep up the walls of the tube where the water surface touches the glass. This tends to increase the surface area of the water, which is opposed by the cohesive forces that try to minimize the surface area.
- Thus, because water has both strong cohesive (intermolecular) forces and strong adhesive forces to glass, it “pulls itself” up a glass capillary tube (a tube with a small diameter).
- The **concave shape of the meniscus** shows that water’s adhesive forces toward the glass are stronger than its cohesive forces.



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15

Liquid Forces

- A **nonpolar liquid** such as mercury shows a **convex meniscus** in a glass tube; example: liquid mercury (see figure).
- This behavior is characteristic of a liquid in which the cohesive forces are stronger than the adhesive forces toward the glass.
- **Viscosity**: a measure of a liquid's resistance to flow.
- Liquids with large intermolecular forces tend to be highly viscous.
- For example: glycerol has an unusually high viscosity mainly because of its high capacity to form hydrogen bonds.



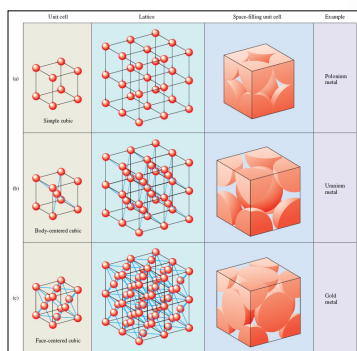
16

Structures and Types of Solids

- **Crystalline solids**: those with a highly regular arrangement of their components.
- **Amorphous solids**: those with considerable disorder in their structures.
- The positions of the components in a crystalline solid are usually represented by a **lattice** - a three-dimensional array of points designating the centers of the components (atoms, ions or molecules) that shows the repetitious pattern of the components.
- The **smallest repeating unit** of the lattice is called the **unit cell**. Thus a particular lattice can be generated by repeating (translating) the unit cell in all three dimensions to form the extended structure.

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17



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18

Three common cubic unit cells & corresponding lattices

Solids

X-Ray Analysis of Solids

- The structures of crystalline solids are most commonly determined by X-ray diffraction.
- Diffraction occurs when beams of light are scattered from a regular array of points or lines where the spacing between the components are comparable to the wavelength of the light.

Types of Crystalline Solids

There are many different types of crystalline solids.

- Common salt (NaCl) is an **ionic solid** that contains Na^+ and Cl^- ions.
- Table sugar (sucrose), on the other hand, is composed of neutral molecules that are dispersed throughout the water when the solid dissolves. Since no ions are present in the solid, the resulting solution does not conduct electricity - **molecular solid**.
- Elements such as graphite, diamond (all pure carbon) and metals are substances that all have atoms occupying the lattice points - **atomic solids**.

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19

Types of Solids


C
Diamond (a)
 Cl^-
 Na^+
Sodium chloride (b)
 H_2O
Ice (c)

FIGURE 16.12: Three types of crystalline solids


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20

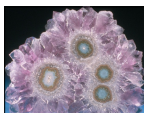
Several Crystalline Solids



Rhodochrosite



Fluorite



Amethyst



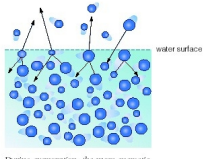
Pyrite

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21

Vapor Pressure and Changes of State

- **Evaporation** is the escape of surface liquid molecules to the gas phase at a temperature below the boiling point.
- This process is endothermic because energy is required to overcome the relatively strong intermolecular forces in the liquid .
- Surface liquid molecules with enough energy to overcome liquid-liquid attraction, separate and escape into the gaseous phase.
- Because container is open, molecules are lost in space where the first liquid layer disappears, then second ... Until no liquid is left.



During evaporation, the more energetic particles escape from the surface leaving the less energetic ones behind.

Vapor Pressure and Changes of State

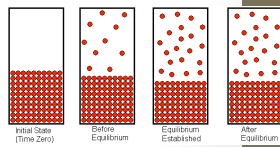
- The energy required to vaporize 1 mole of a liquid at a pressure of 1 atm is called the **standard heat of vaporization** or the standard enthalpy of vaporization and is usually symbolized as $\Delta H_{\text{vap}}^{\circ}$.
- The endothermic nature of vaporization has a great practical significance - one of the most important roles that water plays in our world is to act as a coolant.

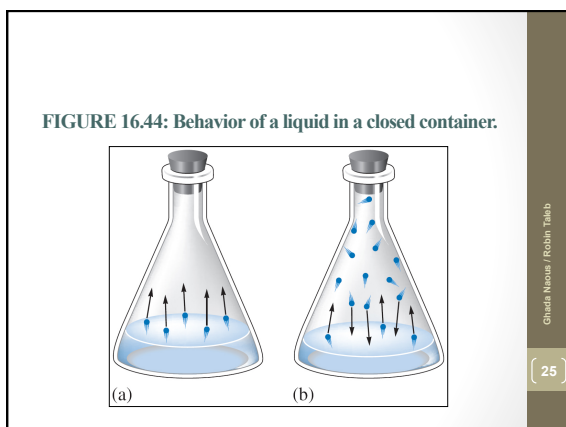
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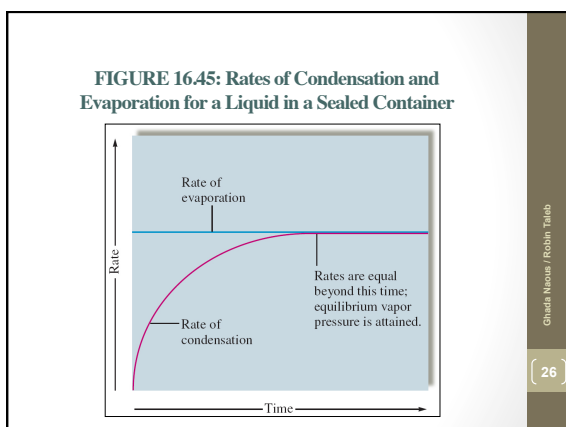
23

Vapor Pressure

- At time $t = 0$, liquid molecules escape to gas (evaporate); No gaseous particles go to liquid (condense).
- At $t = 2$ min: surface liquid molecules go to gas (evaporate), gaseous molecules near surface collide & go to liquid (condense) but rate of evaporation > rate of condensation.
- At $t = 5$ min, liquid molecules go to gas, and gas molecules go to liquid. Rate of evaporation = rate of condensation and an equilibrium state exists.
- These gaseous particles exert a pressure, and since number of gas particles is constant at equilibrium, the pressure is constant at constant temperature.
- The pressure is called the **equilibrium vapor pressure**.







Vapor Pressure Measurement

- Liquid injected into the bottom of a tube of mercury and floats to the surface because mercury is so dense.
- A portion of the liquid evaporates at the top of the column, producing a vapor whose pressure pushes some mercury out of the tube.
- When the system reaches equilibrium, the vapor pressure can be determined from the change in the height of the mercury column.

$P_{atm} = P_{vapor} + P_{Hg\ column}$

so that

$P_{vapor} = P_{atm} - P_{Hg\ column}$

Measures of Vapor Pressure of Three Different Liquids

Vapor Pressure

➤ The **vapor pressure** of a liquid is principally **determined by the strength of the intermolecular forces in the liquid**.

- Liquids with strong intermolecular forces have relatively low vapor pressures because the molecules need high energies to escape to the vapor phase.

➤ **Example:** Although water (18 gmol^{-1}) has a lower molar mass than diethyl ether (74 gmol^{-1}), the strong hydrogen bonding forces that exist among water molecules in the liquid lead to water's much lower vapor pressure compared to non-polar diethyl ether.

➤ In general **substances with large molar masses have relatively low vapor pressures** mainly because of the large dispersion forces.

➤ Measurement of the vapor pressure for a given liquid at several temperatures show **that vapor pressure increases significantly with temperature**.

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28

Vapor Pressure vs Temperature

- The vapor pressure values for water at several temperatures are given in the following table.

➤ We can represent this behavior by the equation:

$$\ln(P_{\text{vap}}) = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T}\right) + C$$

where ΔH_{vap} is the enthalpy of vaporization, R is the universal gas constant, and C is a constant characteristic of a given liquid.

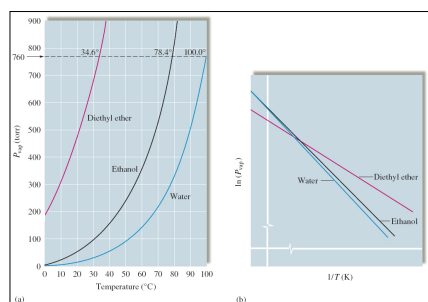
$$\ln K = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$$

TABLE 16.7

The Vapor Pressure of Water as a Function of Temperature

T ($^\circ\text{C}$)	P (torr)
0.0	4.579
10.0	9.209
20.0	17.535
25.0	23.756
30.0	31.824
40.0	55.324
60.0	149.4
70.0	233.7
90.0	525.8

FIGURE 16.48: (a) Vapor pressure of water, ethanol and diethyl ether as a function of temperature, (b) Plots of $\ln(P_{\text{vap}})$ vs $1/T$



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30

Exercise

➤ Using the plots in figure 16.48 (b), determine whether water or diethyl ether has the smaller enthalpy of vaporization.

➤ **Solution:**

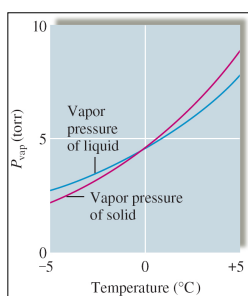
When $\ln(P_{\text{vap}})$ is plotted versus $1/T$, the slope of the resulting straight line is

$$-\frac{\Delta H_{\text{vapor}}}{R}$$

- The line for ether has the smaller slope which corresponds to the smaller value of ΔH_{vap} .

31

FIGURE 16.51: Vapor pressures of solid and liquid water vs temperature



32

Melting Point and Boiling Point

- The melting and boiling points for a substance are determined by the vapor pressures of the solid and liquid states .

TABLE 16.8

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 ₂ O	0	6.01
NaF	992	29.3
NaCl	801	30.2

33

Melting Point and Boiling Point

- The **normal melting point** is defined as *the temperature at which the solid and liquid states have the same vapor pressure under conditions where the total pressure is 1 atm.*
- The **normal boiling point** of a liquid is *the temperature at which the vapor pressure of the liquid is exactly 1 atm.*
- Only when the liquid reaches a temperature at which the pressure of vapor in the spaces in the liquid is 1 atm can bubbles form and boiling occur.

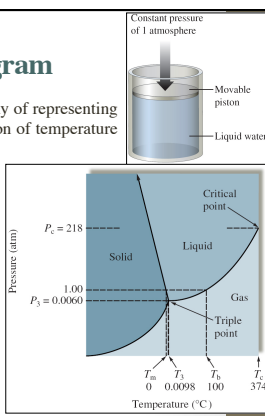
34

Phase Diagram

➤ A **phase diagram** is a convenient way of representing the phases of a substance as a function of temperature and pressure.

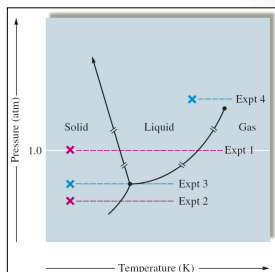
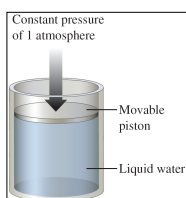
➤ **Example:** The phase diagram of water (Figure 16.55) shows which state exists at a given temperature and pressure.

➤ A phase diagram describes conditions and events for a pure substance in a **closed system** of the type represented in Figure 16.53, where no material can escape into the surrounding and no air is present.



➤ To show how to interpret the phase diagram for water, we will consider heating experiments at several pressures, shown by the dashed lines in Figure 16.56.

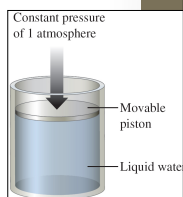
FIGURE 16.56: Plots of various heating experiments on water samples in closed systems



36

> **Experiment 1:**

- Pressure is 1 atm: This experiment begins with the cylinder shown in Figure 16.53 completely filled with ice at a temperature of $-20\text{ }^{\circ}\text{C}$ and with the piston exerting a pressure of 1 atm directly on the ice (there is no air space).
- Since at temperatures below 0°C the vapor pressure of ice is less than 1 atm – which is the constant external pressure on the piston – no vapor is present in the cylinder.
- As the cylinder is heated, ice remains the only component until the temperature reaches 0°C , where ice changes to liquid water as energy is added - the **normal melting point** of water.
- When all the solid has changed to liquid, the temperature rises again.



• **Experiment 1 continued:**

- At this point the cylinder contains only liquid water.
- No vapor is present because the vapor pressure of liquid water under these conditions is less than 1 atm, the constant external pressure on the piston.
- Heating continues until the temperature of the liquid water reaches $100\text{ }^{\circ}\text{C}$. At this point the vapor pressure of liquid water is 1 atm, and boiling occurs ; the liquid changes to vapor.
- This is the normal boiling point of water
- After all liquid has been converted to steam, the temperature rises again as the heating continues.

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38

> **Experiment 2:**

- Pressure is 2 torr: Again ice is the only component in the cylinder at $-20\text{ }^{\circ}\text{C}$. though the pressure exerted by the piston in this case is only 2 torr.
- As heating proceeds the temperature rises to -10°C , where the ice changes directly to vapor through the process of sublimation.
- Sublimation occurs when the vapor pressure of ice is equal to the external pressure, which is in this case is 2 torr.
- No liquid water appears under these conditions because the vapor pressure of liquid water is always greater than 2 torr; thus it cannot exist at this pressure.
- If liquid water were placed in a cylinder at such low pressure, it would vaporize immediately.

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39

> **Experiment 3:**

- Pressure is 4.558 torr: Again ice is the only component in the cylinder at -20 °C. Here, the pressure exerted on the ice by the piston is 4.588 torr.
- As the cylinder is heated, no new phase appears until the temperature reaches 0.0098 °C.
- At this point, called the **triple point**, solid and liquid water have identical vapor pressures of 4.588 torr.
- Thus at 0.0098 °C and 4.588 torr - the **triple point - all three states of water are present**. In fact, only under these conditions can all three states of water co-exist.

40

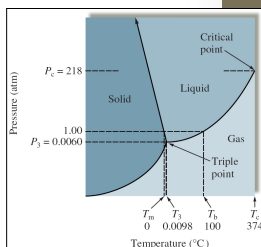
> **Experiment 4:**

- Pressure is 225 atm: Liquid water is in the cylinder at 300 °C; the pressure exerted by the piston on the water is 225 atm.
- Liquid water can be present at this temperature because of the high external pressure.
- As the temperature increases, something happens that we did not observe in the first three experiments: the liquid goes through an intermediate “fluid” region, which is neither true liquid nor vapor.
- The **critical temperature** is defined as the temperature above which the vapor cannot be liquefied no matter what pressure is applied.
- The **critical pressure** is the pressure required to produce liquefaction at the critical temperature.

41

> **Experiment 4 continued:**

- Together the critical temperature and critical pressure define the **critical point**.
- For water, the critical point occurs at 374 °C and 218 atm.
- Note that the liquid/vapor line on the phase diagram for water **ends** at the critical point. This point to another transition from one state to another involves the intermediate “fluid” region just described.



Phase diagram for Water

- **Note that the solid/liquid boundary line has a negative slope.**
This means that the melting point of water decreases as the external pressure increases. This unusual behavior, which is opposite to that observed for most substances, occurs because the *density of ice is less than that of liquid water at the melting point*. Thus, when liquid water freezes, its volume increases. The solid/liquid line has no upper limit.
- **The freezing point of water is less than 0°C when the pressure is greater than 1 atm.**
- The lower density of ice has other implications:
- When water freezes in a pipe or an engine block, it expands and breaks the container. For this reason water pipes are insulated in cold climates and antifreeze is used in water-cooled engines.
- The ice formed on rivers and lakes float, providing a layer of insulation that helps prevent bodies of water from freezing solid in the winter.

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43

FIGURE 16.57: Effect of pressure on melting point

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44

TABLE 16.9
Boiling Point of Water at Various Locations

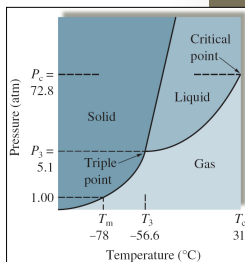
Location	Feet Above Sea Level	P_{atm} (torr)	Boiling Point (°C)
Top of Mt. Everest, Tibet	29,028	240	70
Top of Mt. McKinley, Alaska	20,320	340	79
Top of Mt. Whitney, Calif.	14,494	430	85
Leadville, Colo.	10,150	510	89
Top of Mt. Washington, N.H.	6,293	590	93
Boulder, Colo.	5,430	610	94
Madison, Wis.	900	730	99
New York City, N.Y.	10	760	100
Death Valley, Calif.	-282	770	100.3

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45

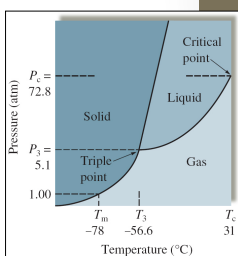
The Phase Diagram for Carbon Dioxide

- The phase diagram for carbon dioxide (CO₂) (Figure 16.58) differs significantly from that for water.
- The solid/liquid line has a positive slope, since solid CO₂ is more dense than liquid CO₂.
- The triple point for CO₂ occurs at 5.1 atm and -56.6°C, and the critical point occurs at 72.8 atm and 31°C.
- At 1 atm, solid CO₂ sublimates at -78°C, a property that leads to its common name, *dry ice*.

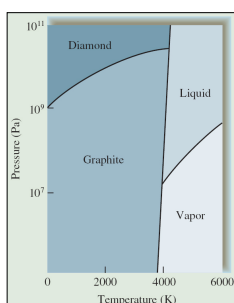


The Phase Diagram for Carbon Dioxide

- No liquid phase occurs under normal atmospheric conditions, making dry ice a convenient coolant.
- CO₂ is often used in fire extinguishers, where it exists as a liquid at 25°C under high pressures.
- Liquid CO₂ released from the extinguisher into the environment at 1 atm immediately changes to a vapor.
- Being heavier than air, this vapor smothers the fire by keeping oxygen away from flame.
- The liquid/vapor transition is highly endothermic, so cooling also results, which helps to put out the fire.



Phase Diagram for Carbon



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