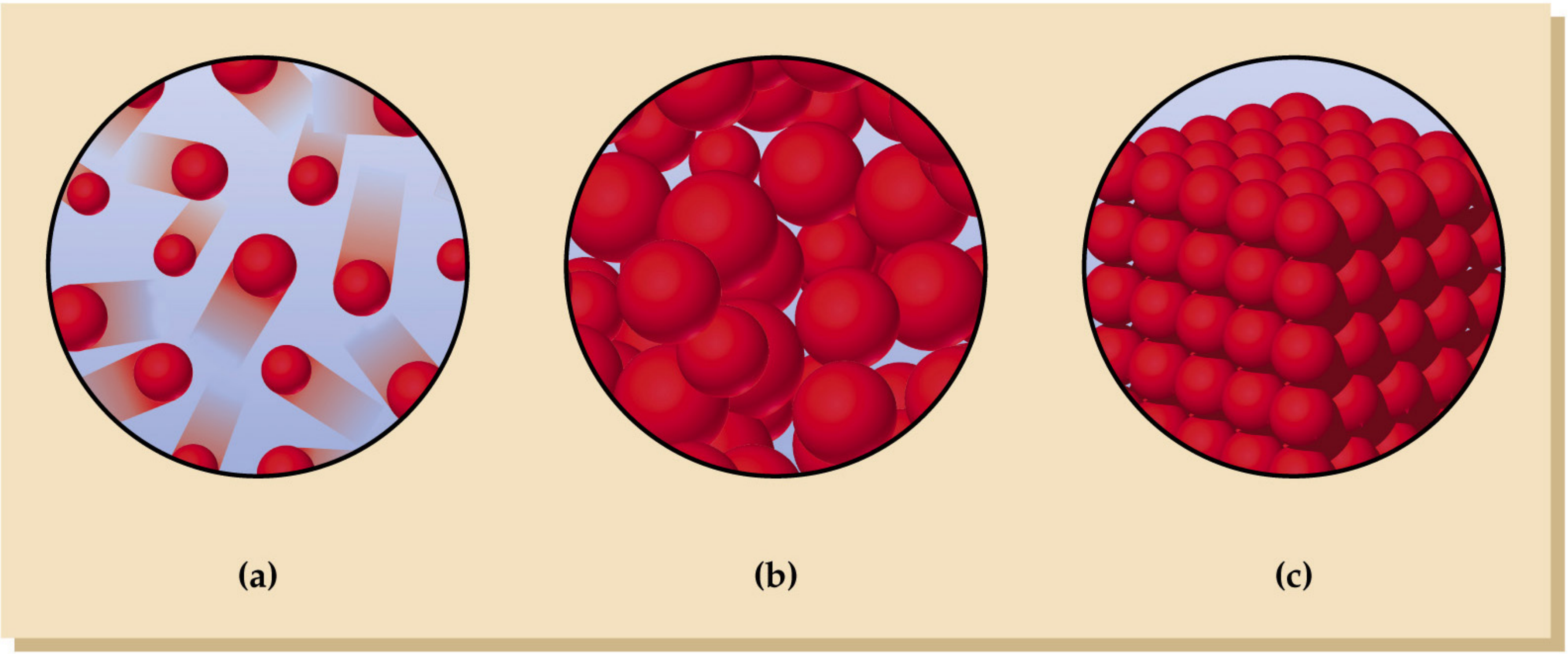
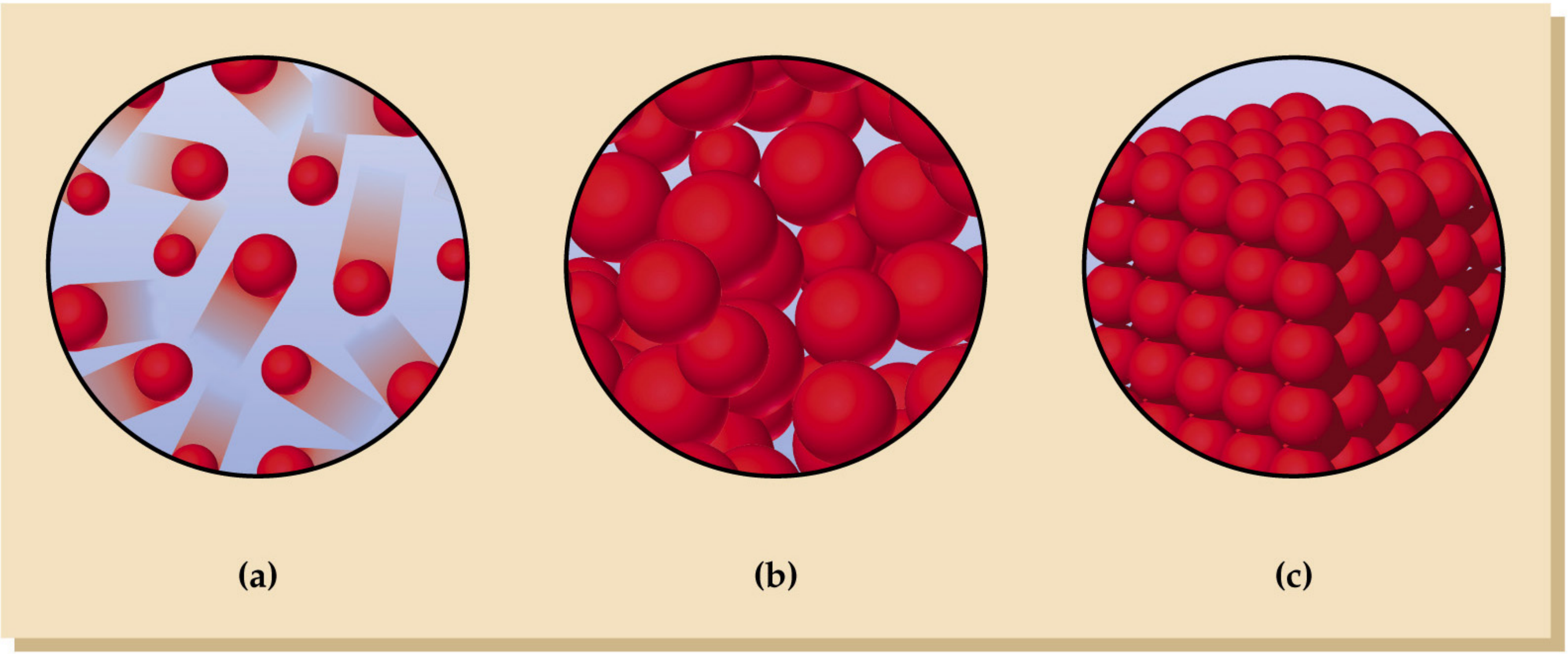
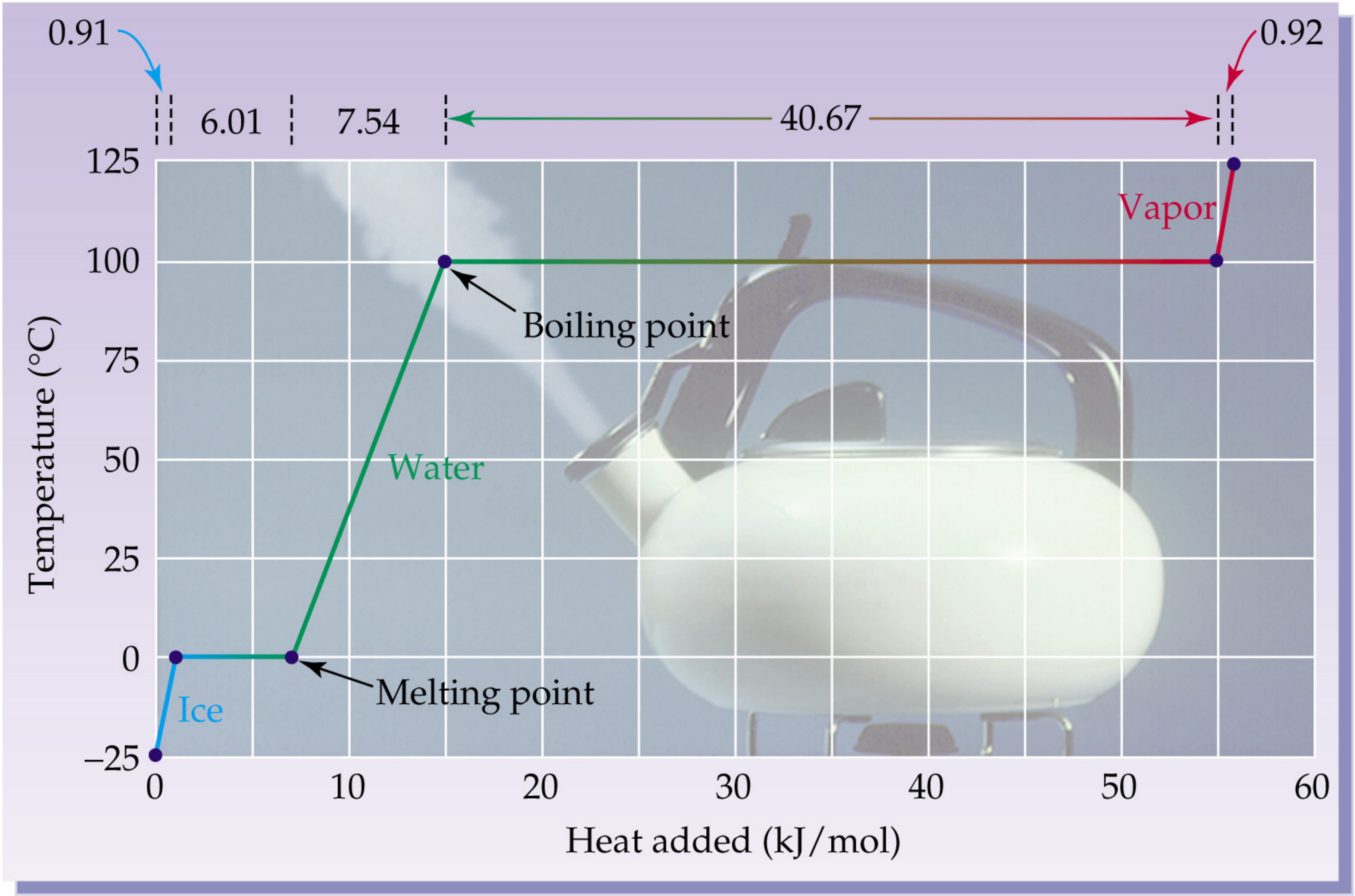
Chapter 10 Liquids, Solids and Phase Changes



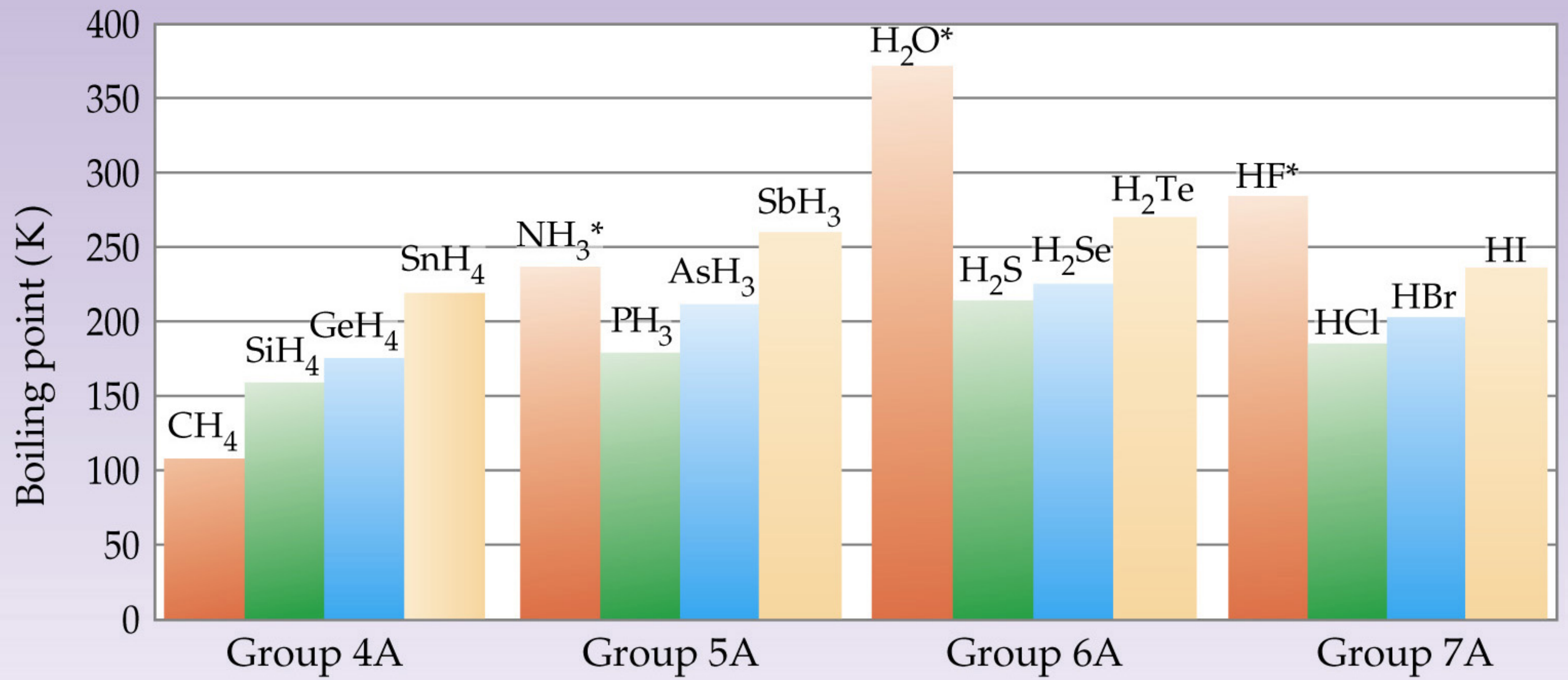
The three phases of matter: solids, liquids and gases



Phase change properties of pure water at 1 atm pressure



What is a boiling point? What does it measure?



*The boiling points generally increase with increasing molecular mass down a group of the periodic table, but the hydrides of nitrogen (NH_3), oxygen (H_2O), and fluorine (HF) have abnormally high boiling points because these molecules form hydrogen bonds.

H_2O: a unique substance

Hydrogen bonds: hydrogen attached to an oxygen in particular, is capable of causing association. The association is electrostatic in nature and leads to compounds that have significantly more association than one would otherwise expect.

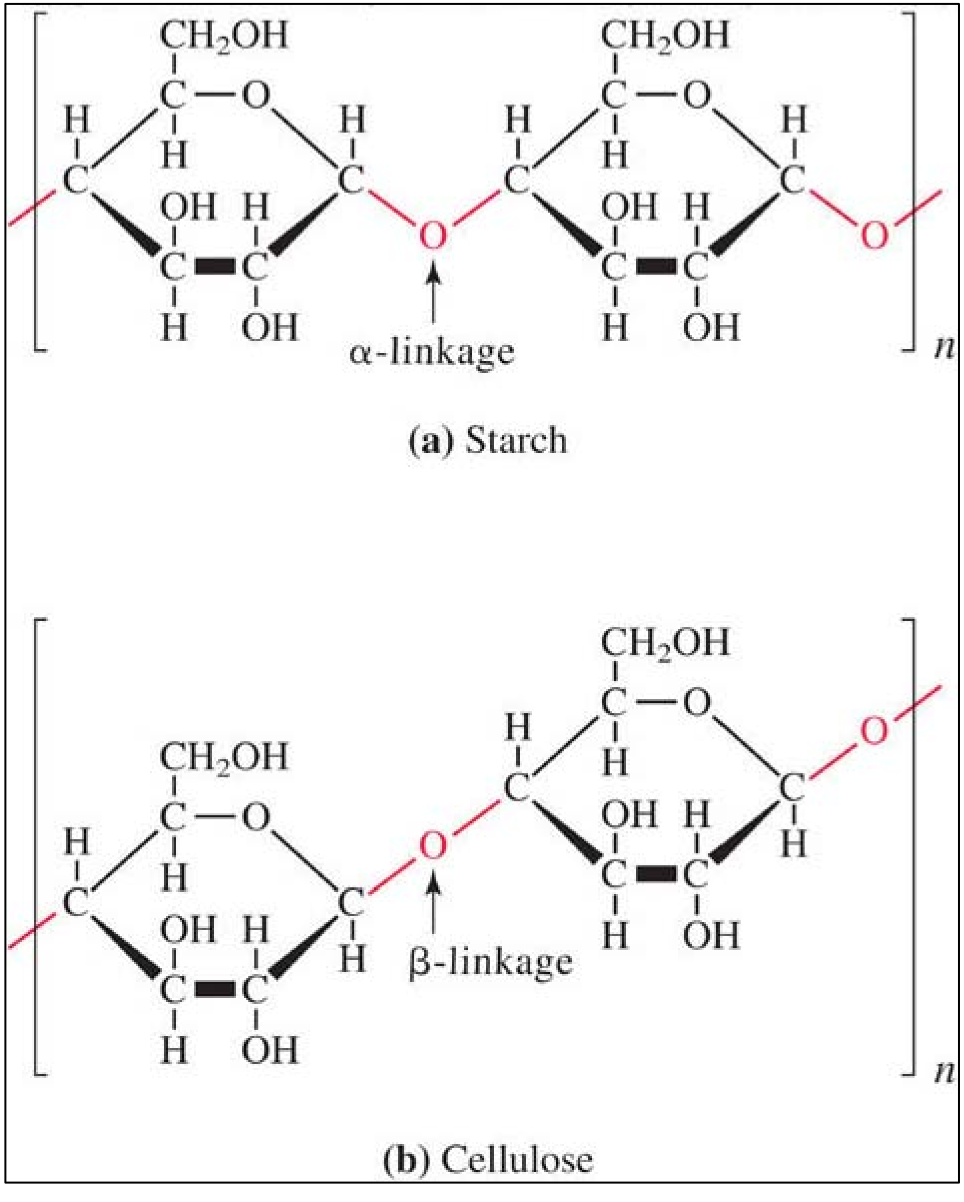
Compounds that form hydrogen bonds have a form of chemical stickyness not found in other materials.

Significance: Self association is fundamental to understanding all biological processes and more often than not, hydrogen bonding is responsible for this self association.

A few examples:

1. reproduction of the genetic code
2. antigen-antibody response
3. transport across cell membranes
4. What hold paper together?

When many sugars are linked together you have polysaccharides, which are natural polymers:



(a) Starch

(b) Cellulose

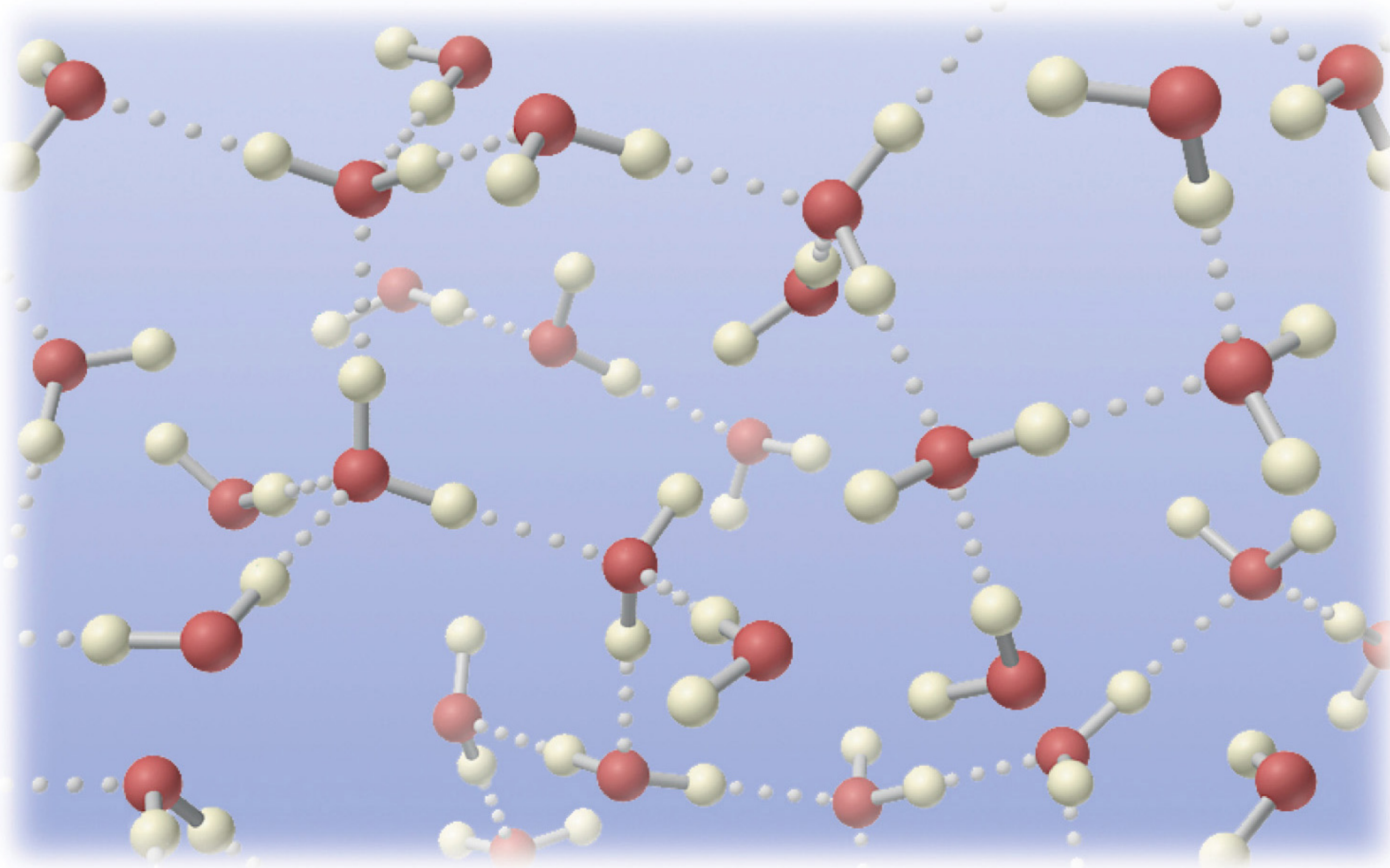
Because the single sugars can be either α or β, two different linkages arise.

When glucose polymerizes,

an α – linkage makes starch

and a β – linkage makes cellulose.

oxygen: red; hydrogen: white



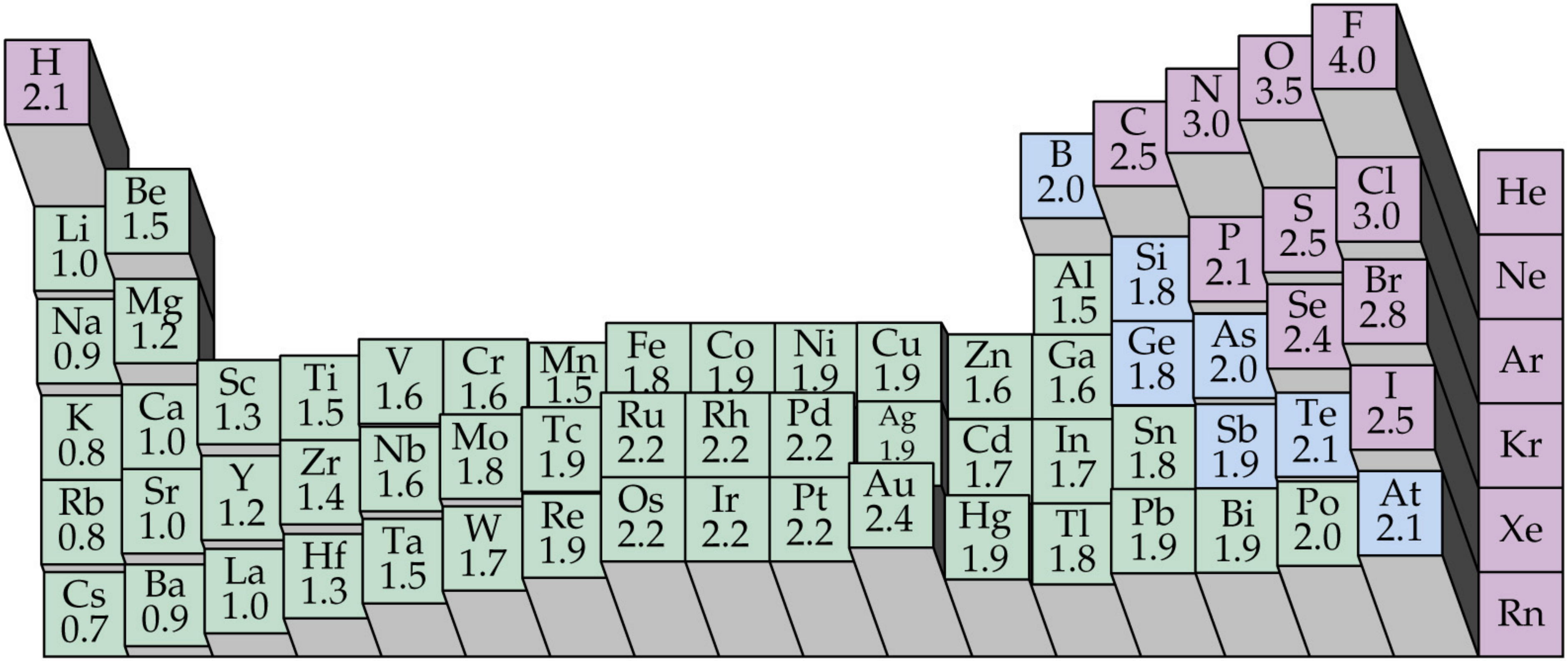
Hydrogen bonding in H_2O

Other types of weak bonds leading to some self association:

1. Dipole-dipole interactions: forces associated with non-symmetrical molecules especial those that have atoms bonded with large electronegativity differences.

2. London dispersion forces: the weakest of all the forces we encounter. These forces are responsible for our ability to condense substances such as methane, N_2 , He. These forces are often encountered in symmetrical molecules and in molecule in which the electrons are shared equally.

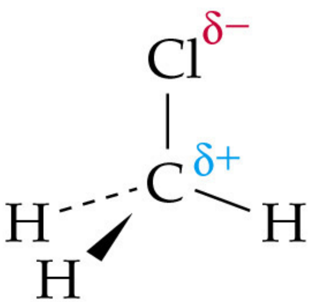
What is the experimental evidence for these forces?



Electronegativities

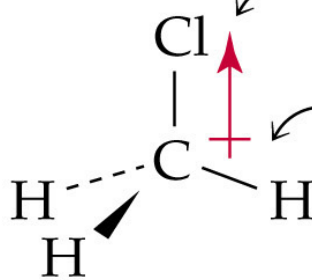
TABLE 10.5 A Comparison of Intermolecular Forces

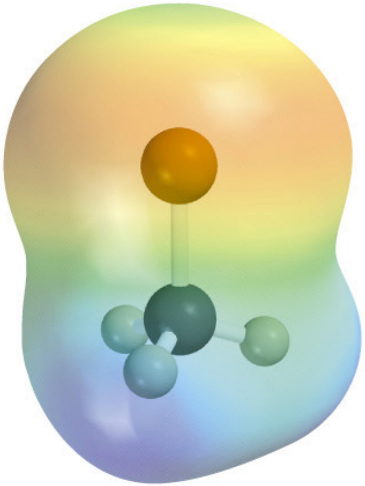
Force	Strength	Characteristics
Ion–dipole	Moderate (10–50 kJ/mol)	Occurs between ions and polar solvents
Dipole–dipole	Weak (3–4 kJ/mol)	Occurs between polar molecules
London dispersion	Weak (1–10 kJ/mol)	Occurs between all molecules; strength depends on size, polarizability
Hydrogen bond	Moderate (10–40 kJ/mol)	Occurs between molecules with O–H, N–H, and F–H bonds



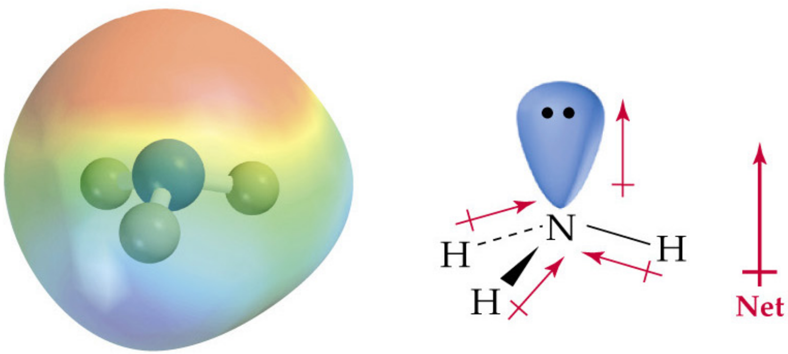
Chloromethane, CH_3Cl

or

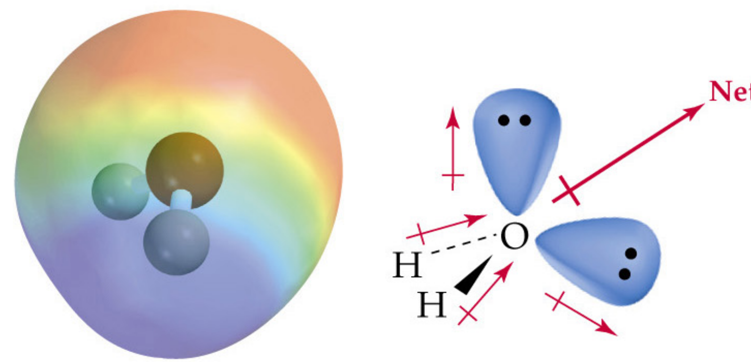




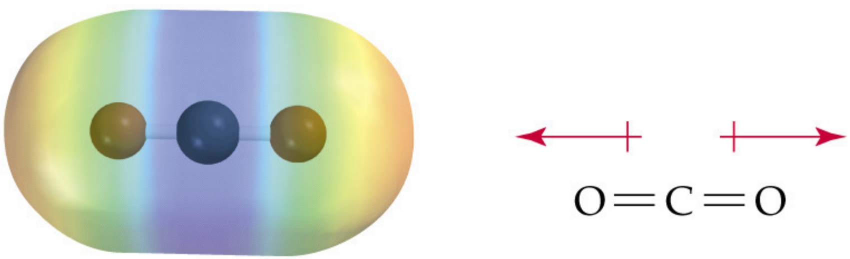
a dipole is a vector, that is it has both magnitude and direction



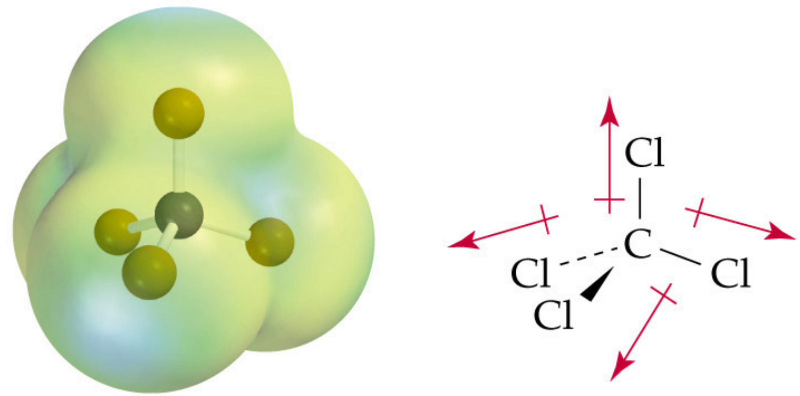
Ammonia (μ = 1.47 D)



Water (μ = 1.85 D)



Carbon dioxide (μ = 0)



Tetrachloromethane (μ = 0)

TABLE 10.1 Dipole Moments of Some Common Compounds

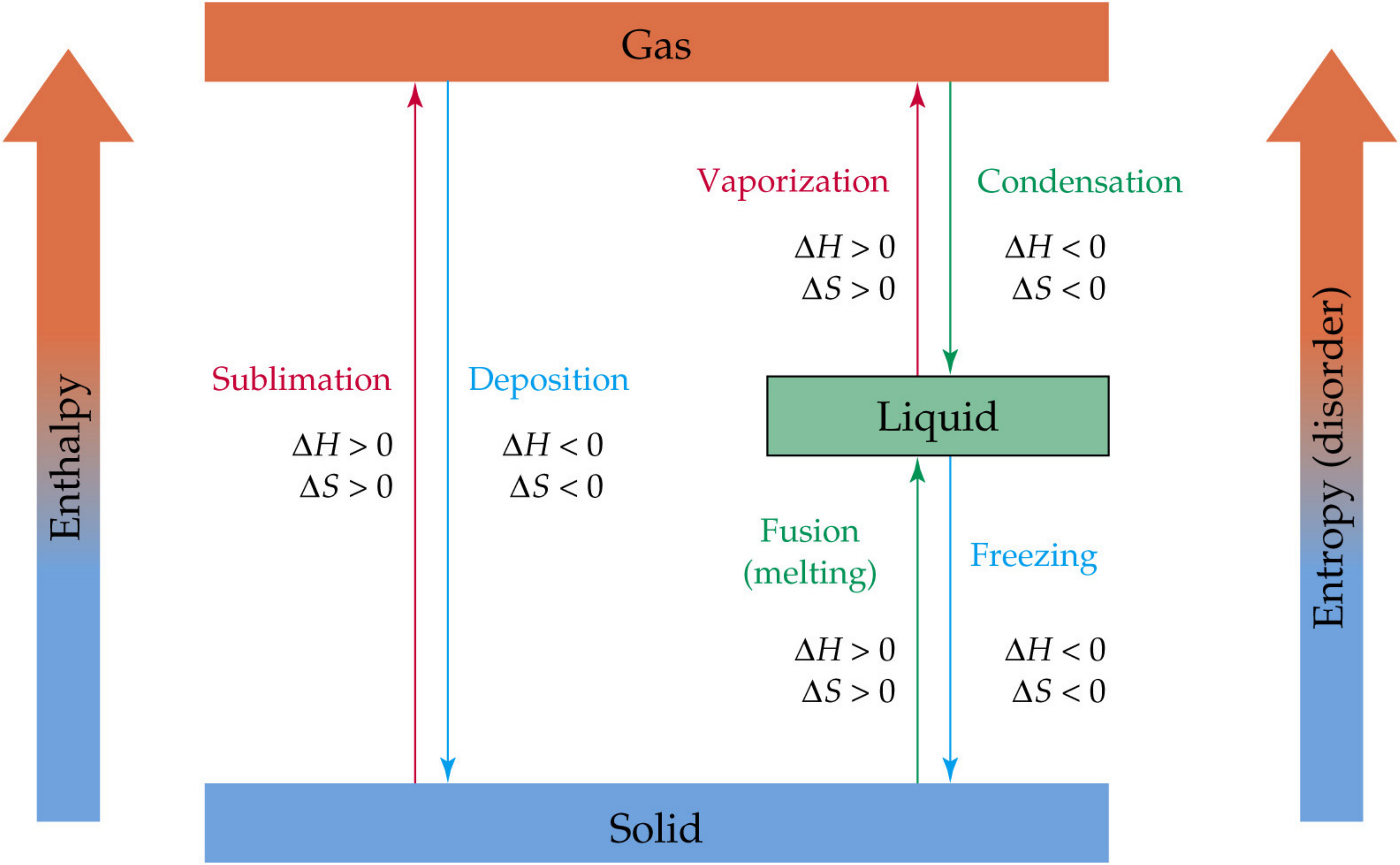
Compound	Dipole Moment (D)
NaCl*	9.0
CH_3Cl	1.87
H_2O	1.85
NH_3	1.47
CO_2	0
CCl_4	0

*Measured in the gas phase

TABLE 10.2 Comparison of Molecular Masses, Dipole Moments, and Boiling Points

Substance	Mol Mass (amu)	Dipole Moment (D)	bp (K)
$CH_3CH_2CH_3$	44.10	0.1	231
CH_3OCH_3	46.07	1.3	248
CH_3Cl	50.49	1.9	249
CH_3CN	41.05	3.9	355

Dipole moment is define as charge separation*distance of separation; dipole moments are vectors is so far as they have magnitude and direction.


Gas
Enthalpy
Entropy (disorder)
Sublimation
$\Delta H > 0$
$\Delta S > 0$
Deposition
$\Delta H < 0$
$\Delta S < 0$
Vaporization
$\Delta H > 0$
$\Delta S > 0$
Condensation
$\Delta H < 0$
$\Delta S < 0$
Liquid
Fusion (melting)
$\Delta H > 0$
$\Delta S > 0$
Freezing
$\Delta H < 0$
$\Delta S < 0$
Solid

Fusion enthalpy: the amount of heat necessary to convert a fixed amount of solid at its melting temperature to the liquid at the same temperature. Units: J/mol; J/g

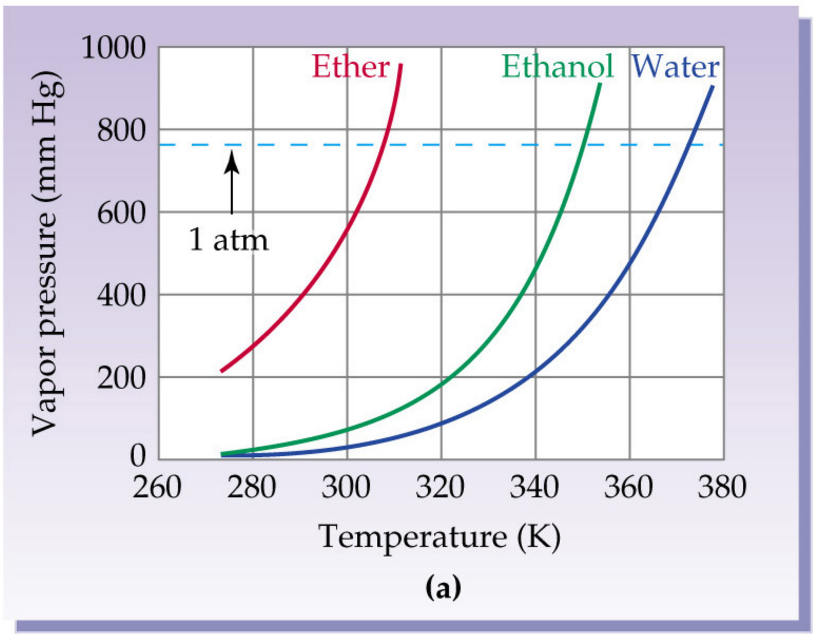
Vaporization enthalpy: the amount of heat necessary to convert a fixed amount of liquid at its boiling temperature to the gas at the same temperature. Units: J/mol; J/g

TABLE 10.7 Heats of Fusion and Heats of Vaporization for Some Common Compounds

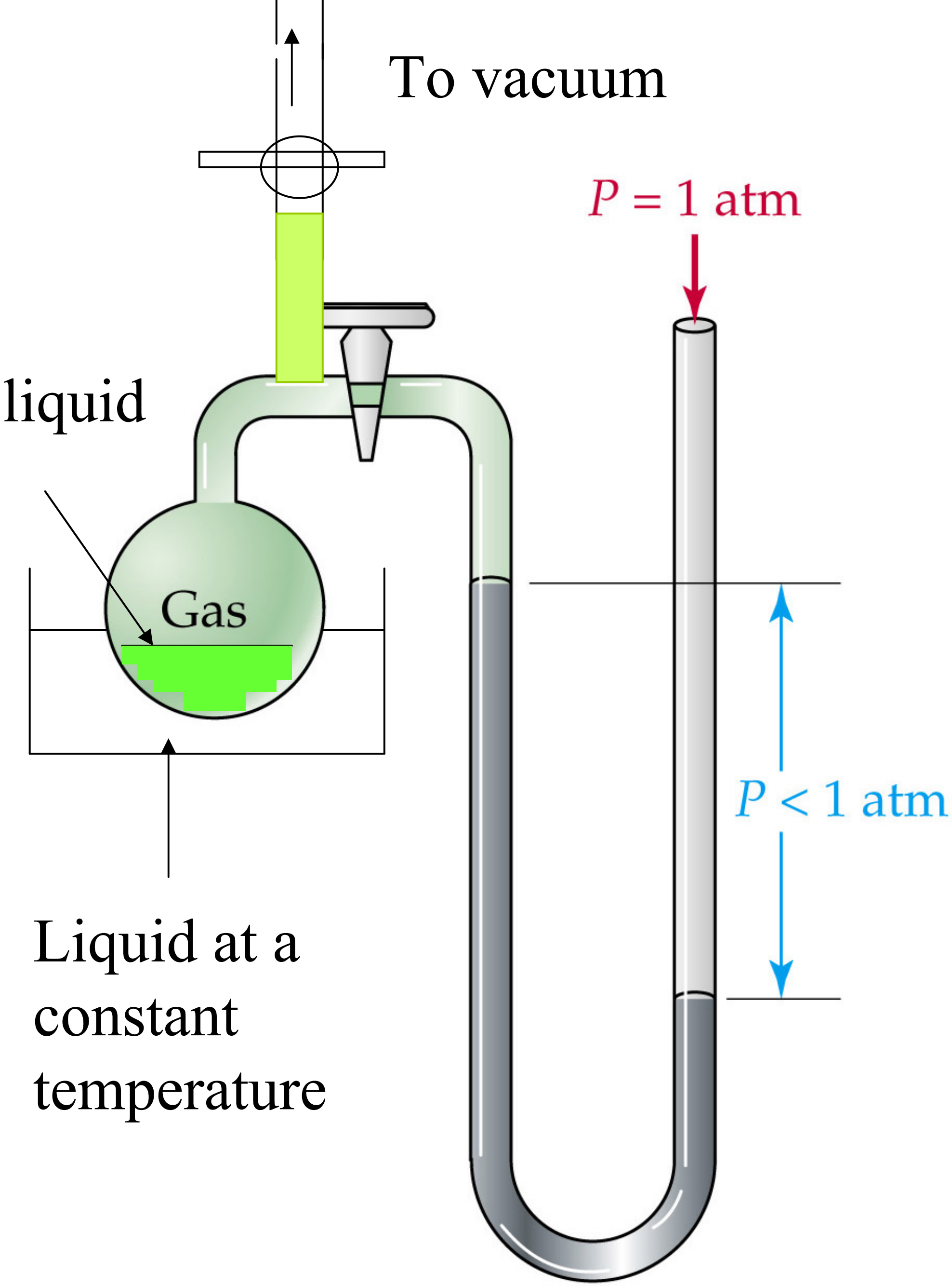
Name	Formula	ΔH_{fusion} (kJ/mol)	ΔH_{vap} (kJ/mol)
Ammonia	NH_3	5.97	23.4
Benzene	C_6H_6	9.95	30.8
Ethanol	C_2H_5OH	5.02	38.6
Helium	He	0.02	0.10
Mercury	Hg	2.33	56.9
Water	H_2O	6.01	40.67

Normal boiling temperature: the temperature at which the vapor pressure of the liquid equals 1 atm

How does vapor pressure vary with temperature?



How do we measure vaporization enthalpy?

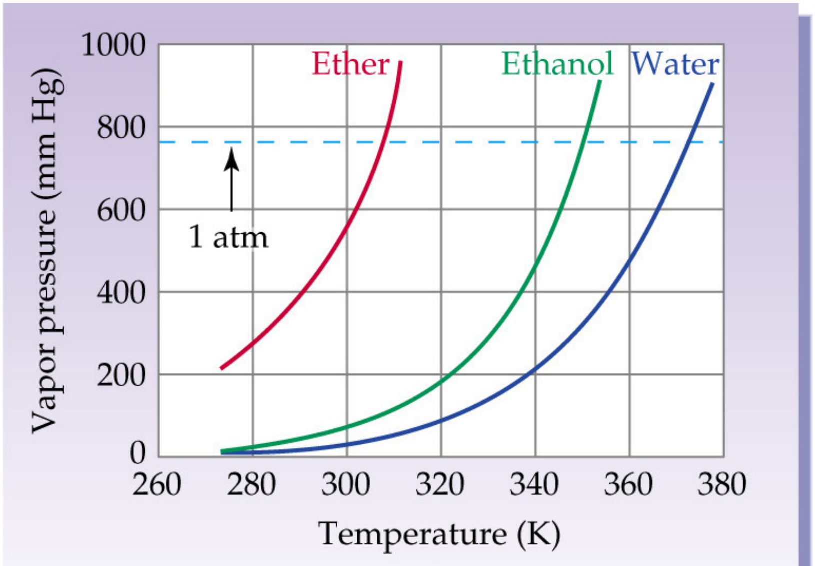


(a)

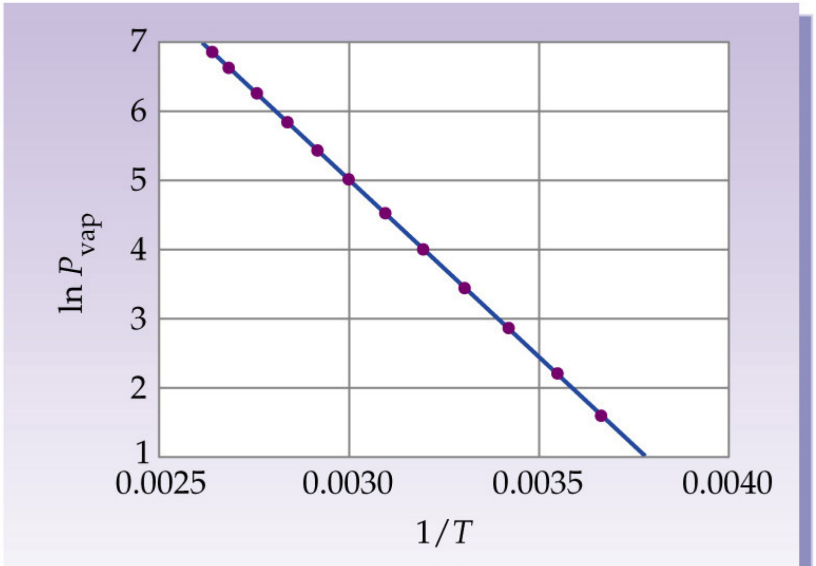
One way of measuring vapor pressures

1. Cool the liquid to a very low temperature
2. Open the valve to vacuum to remove any air
3. Close the valve to the vacuum
4. Replace the liquid with a bath at a constant temperature and record the change in the different levels of mercury

Plot ln(P) against 1/T where T is in Kelvin



(a)



(b)

What's ln(P)? Whats' log(P)?

Logarithms: expressing a number in the form of an exponent

number	log	logarithm base 10
10	1	10^1
100	2	10^2
1000	3	10^3

number	ln	logarithm base 2.718
2.718	1	$2.718^1 = 2.718$
7.39	2	$2.718^2 = 7.39$
20.09	3	$2.718^3 = 20.09$

$$\ln(x) = 2.303\log(x)$$

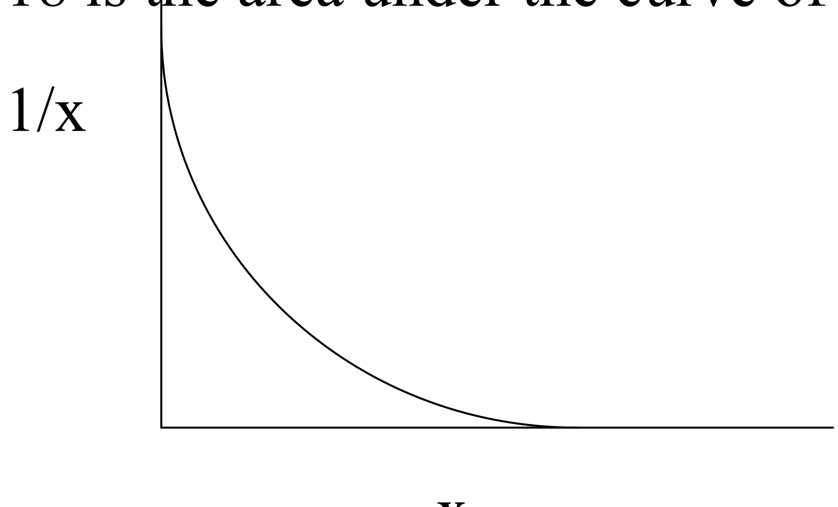
the log of the number 200

$\log(200) = 2.3$ $10^{2.3} = 200$; log uses the base 10

$\ln(200) = 5.2983$; $2.718^{5.2983}$

Where does the number 2.718 come from?

2.718 is the area under the curve of 1/x where x goes from 0 to infinity



How do we measure vaporization enthalpy?

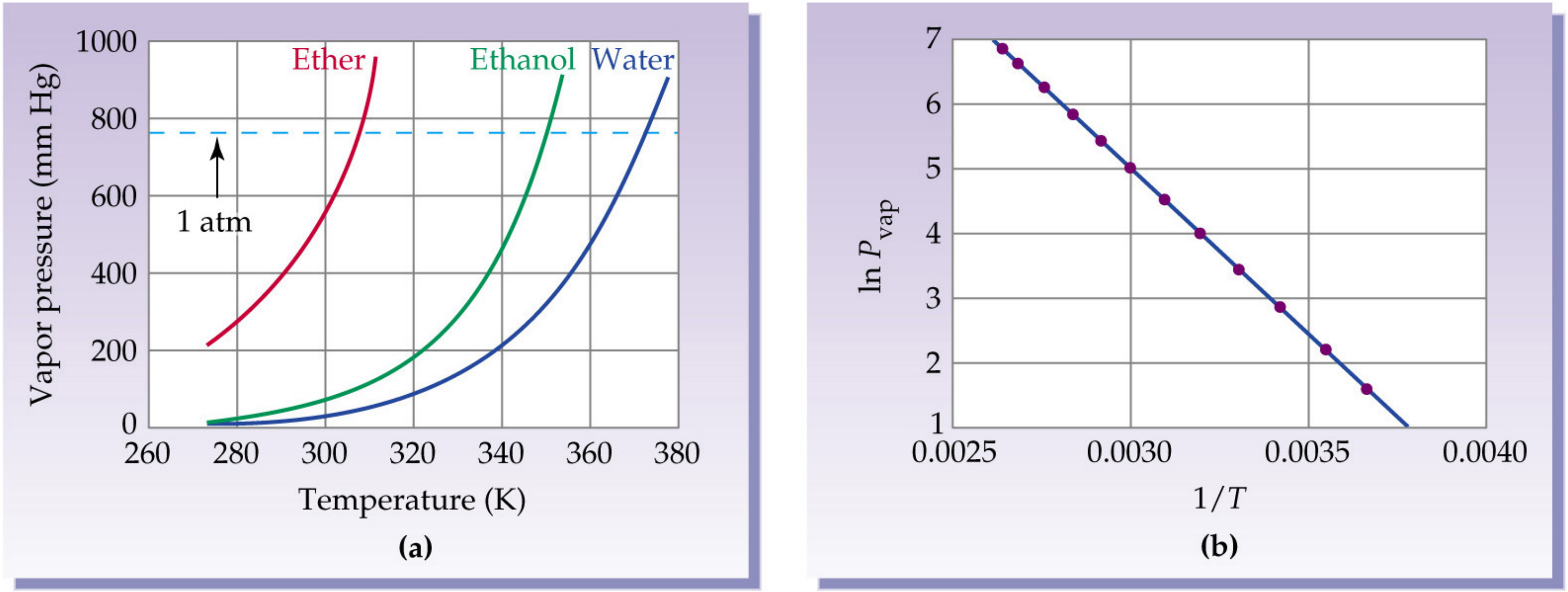
It has been found that by measuring the vapor pressure of a liquid as a function of temperature, an exponential increase in vapor pressure is observed.

Furthermore, it has bee also found that by plotting the logarithm of vapor pressure as a function of 1/T where T is in K, a linear plot is obtained.

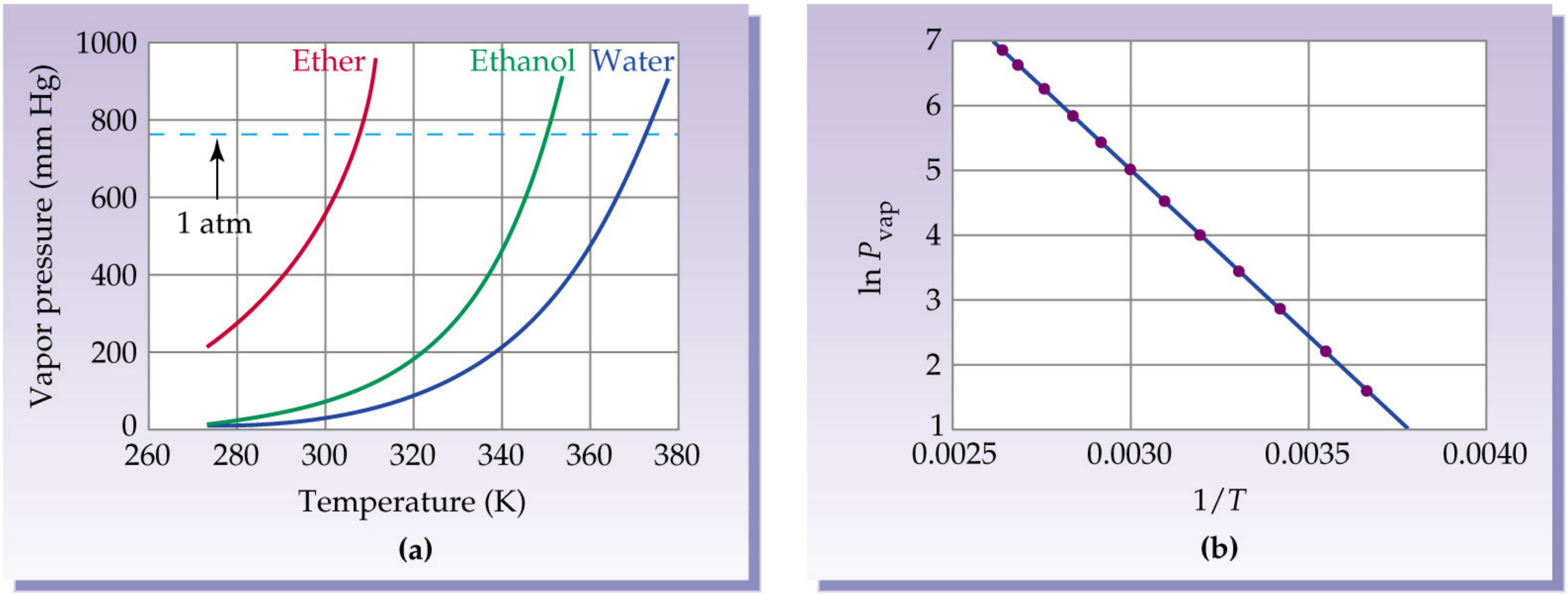
The slope of the line has been found to equal to $-\Delta H_{vap}/R$ where R is the gas constant, 1.987 cal/mol or 8.314 J/mol

TABLE 10.8 Vapor Pressure of Water at Various Temperatures

Temp (K)	P_{vap} (mm Hg)	ln P_{vap}	$1/T$	Temp (K)	P_{vap} (mm Hg)	ln P_{vap}	$1/T$
273	4.58	1.522	0.003 66	333	149.4	5.007	0.003 00
283	9.21	2.220	0.003 53	343	233.7	5.454	0.002 92
293	17.5	2.862	0.003 41	353	355.1	5.872	0.002 83
303	31.8	3.459	0.003 30	363	525.9	6.265	0.002 75
313	55.3	4.013	0.003 19	373	760.0	6.633	0.002 68
323	92.5	4.527	0.003 10	378	906.0	6.809	0.002 65



(a) (b)



We can express this line using the general equation for a straight line:

$$y = mx + b$$

in this case y = lnP, and x = 1/T; the slope of the line is found to be

$-\Delta H_{vap}/R$

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

$$\begin{array}{ccccccc} \uparrow & & \uparrow & \uparrow & & \uparrow \\ y & = & m & x & + & b \end{array}$$

Clausius Clapeyron Equation

ln(P) = 2.303log(P)

ΔH_{vap} = vaporization enthalpy

R=gas constant 1.987 cal/(K mol); 8.314 J/(mol K); 0.0821Latm/(K mol)

TABLE 10.8	Vapor Pressure of Water at Various Temperatures						
Temp (K)	**P_{vap} (mm Hg)**	**ln P_{vap}**	**1/T**	**Temp (K)**	**P_{vap} (mm Hg)**	**ln P_{vap}**	**1/T**
293	17.5	2.862	0.003 41	353	355.1	5.872	0.002 83
303	31.8	3.459	0.003 30	363	525.9	6.265	0.002 75

Let calculate the vaporization enthalpy of water at T = 298 K:

$\ln P_1 = -\Delta H_{vap} / [1/T_1]/R + b$

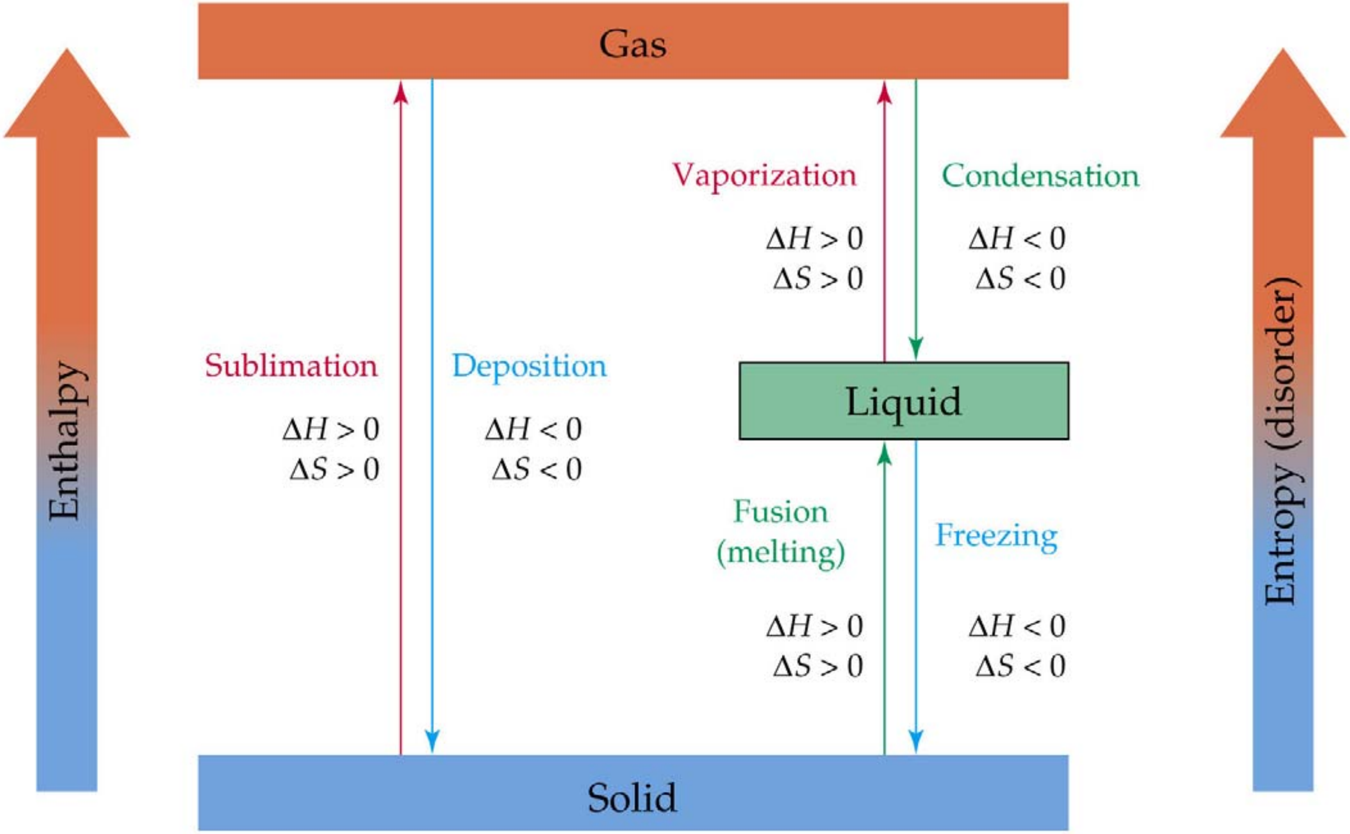
$\ln P_2 = -\Delta H_{vap} [1/T_2] /R + b$ lets subtract the first eq from the second

$\ln P_2 - \ln P_1 = -\Delta H_{vap} [1/T_2 - 1/T_1] /R$

$3.459 - 2.862 = -\Delta H_{vap} [1/303 - 1/293] /R$

$.597 * 8.314 J/(mol K) = .00011 \Delta H_{vap}$

ΔH_{vap} = 45120 J/mol at 298 K; the text reports 40670 at 373 K



We have now learned how to experimentally calculate ΔH_{vap};

ΔH_{sub} is calculated in the same way using the same equation.

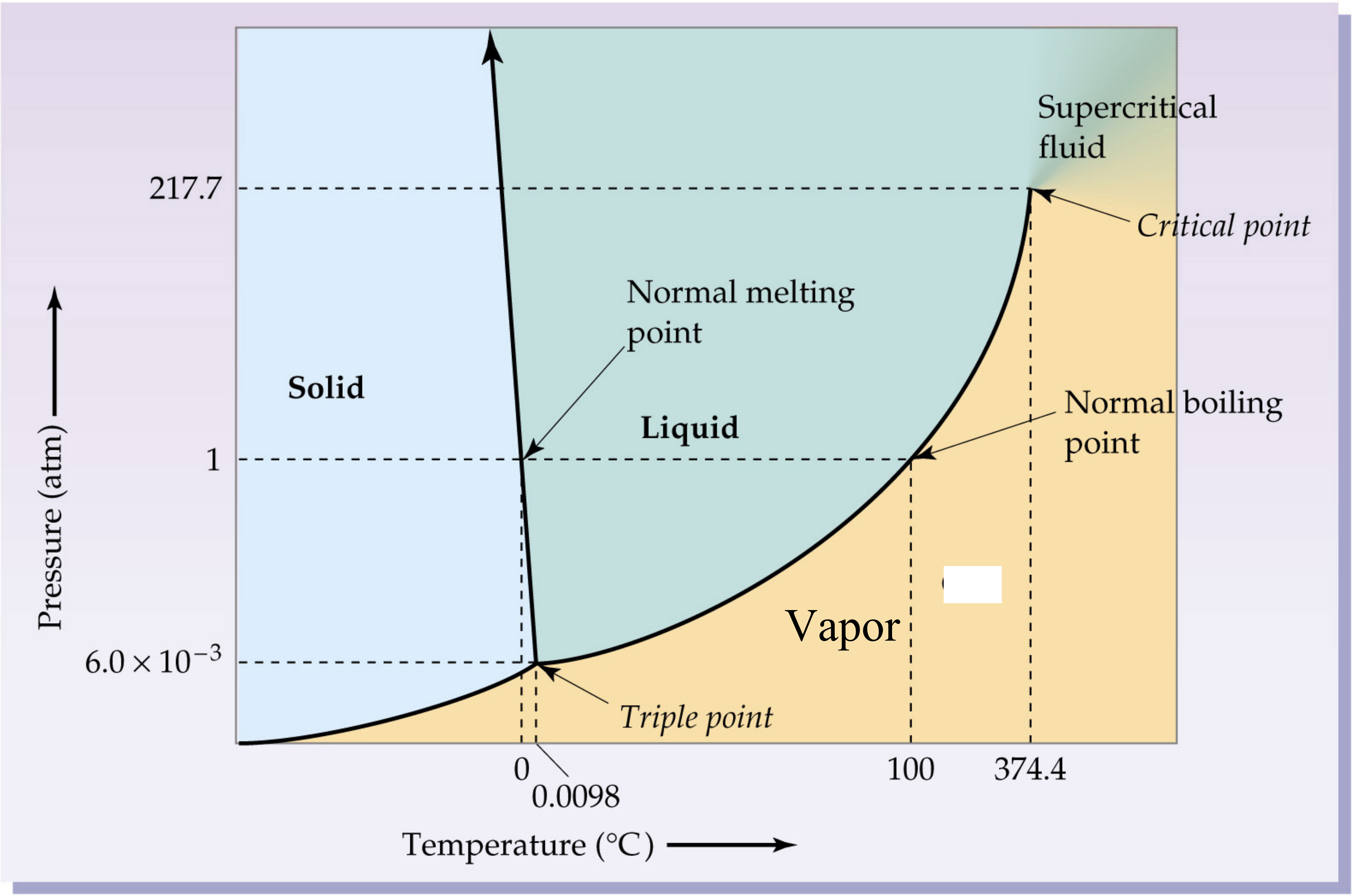
We calculate ΔS_{vap} for a phase change at constant temperature?

$\Delta S_{vap} = \Delta H_{vap}/T_b$ where ΔH_{vap} is the value measured at the boiling point T_b; likewise $\Delta H_{fus} = \Delta H_{fus}/T_{fus}$ where T_{fus} is the melting point

The text reports 40670 at 373 K; since the boiling of water takes place at a constant temperature, $\Delta G = 0$; the entropy change

$$\Delta S_{vap} = \Delta H_{vap}/T_b = 40670/373 = 109 \text{ J/(mol K)}$$

$$\Delta S_{fus} = \Delta H_{fus}/T_{fus} = 6010/273 = 22.0 \text{ J/(mol K)}$$



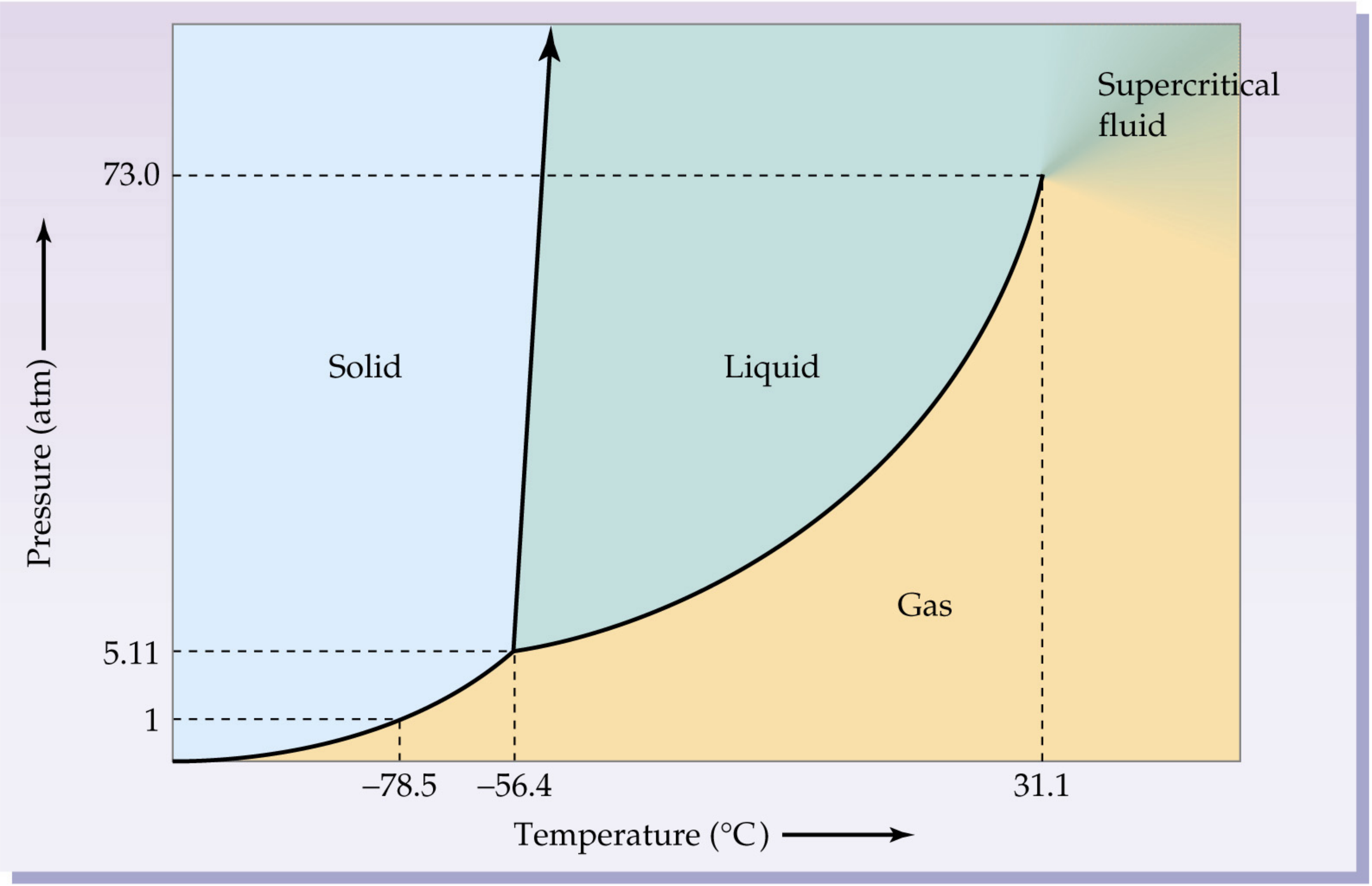
Phase Diagram of Water

Nitrogen bp = -186 °C

Dry Ice (CO_2) bp = -77 °C ?

-77 °C is the temperature at which the vapor pressure of CO_2 = 1 atm

Why doesn't Dry Ice melt?



Phase Diagram of CO_2

Viscosity and surface tension

Viscosity relates to how freely molecules can flow over each other; is related to the nature of the intermolecular forces present in liquid.

Surface tension is the term used to describe the unequal forces acting on those molecules on a surface that are not surrounded by other molecules; causes formation of spheres

TABLE 10.6 Viscosities and Surface Tensions of Some Common Substances at 20°C

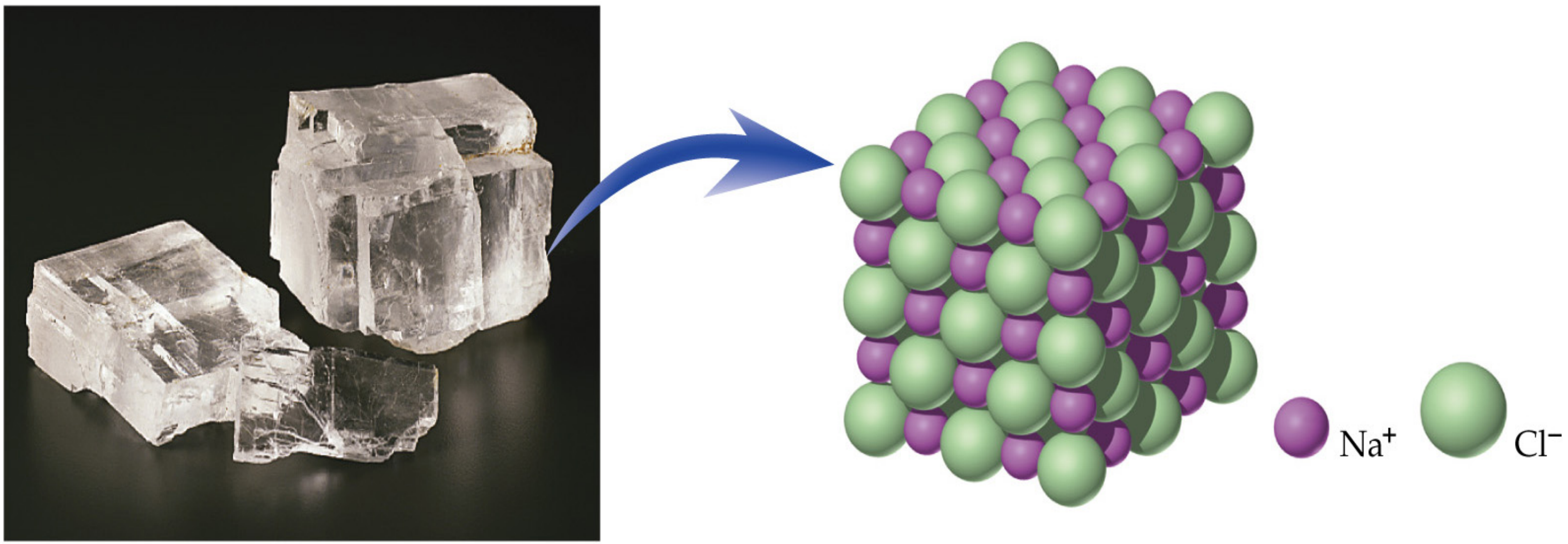
$N = kg^{*}m/s^{2}$; force= mass*accelation

Name	Formula	Viscosity ($N \cdot s/m^2$)	Surface Tension (J/m^2)
Pentane	C_5H_{12}	2.4×10^{-4}	1.61×10^{-2}
Benzene	C_6H_6	6.5×10^{-4}	2.89×10^{-2}
Water	H_2O	1.00×10^{-3}	7.29×10^{-2}
Ethanol	C_2H_5OH	1.20×10^{-3}	2.23×10^{-2}
Mercury	Hg	1.55×10^{-3}	4.6×10^{-1}
Glycerol	$C_3H_5(OH)_3$	1.49	6.34×10^{-2}

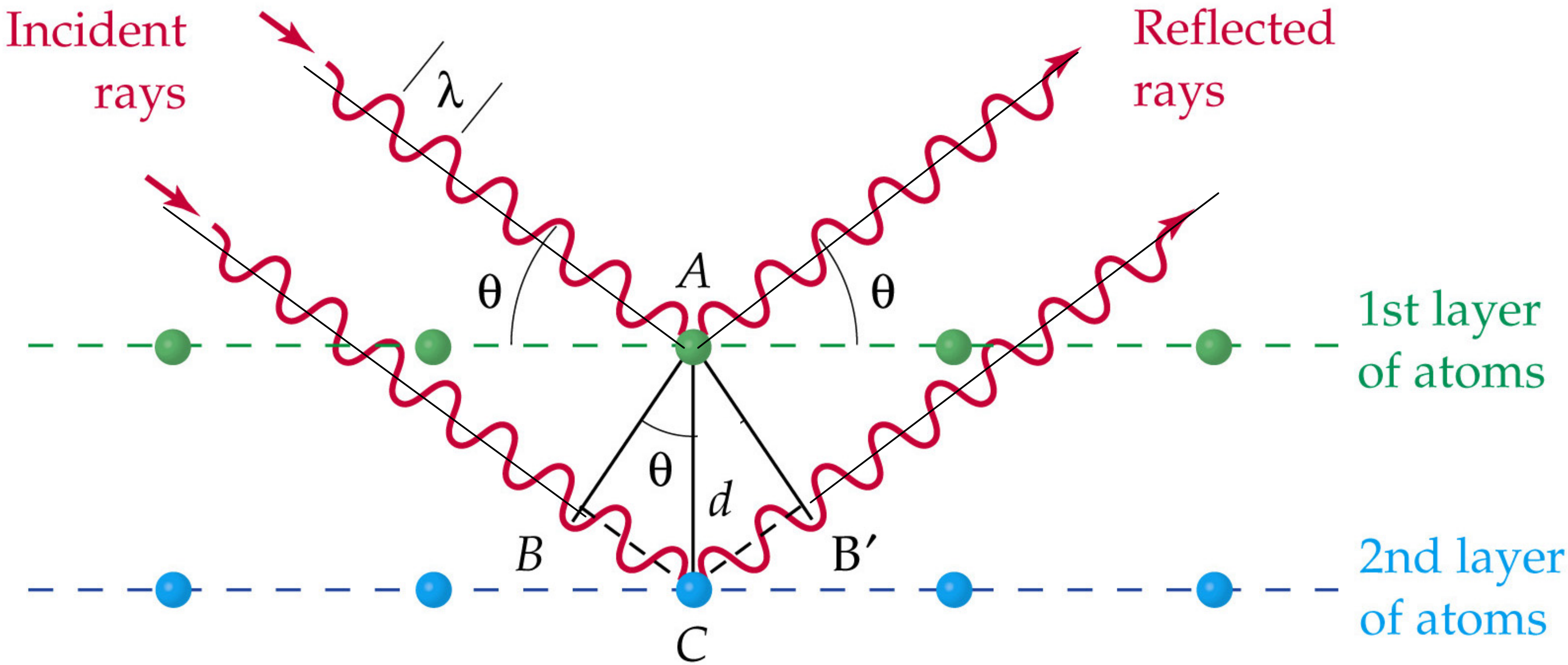
Packing in solids

How is structure in the crystalline state determined?

NaCl cubic structure

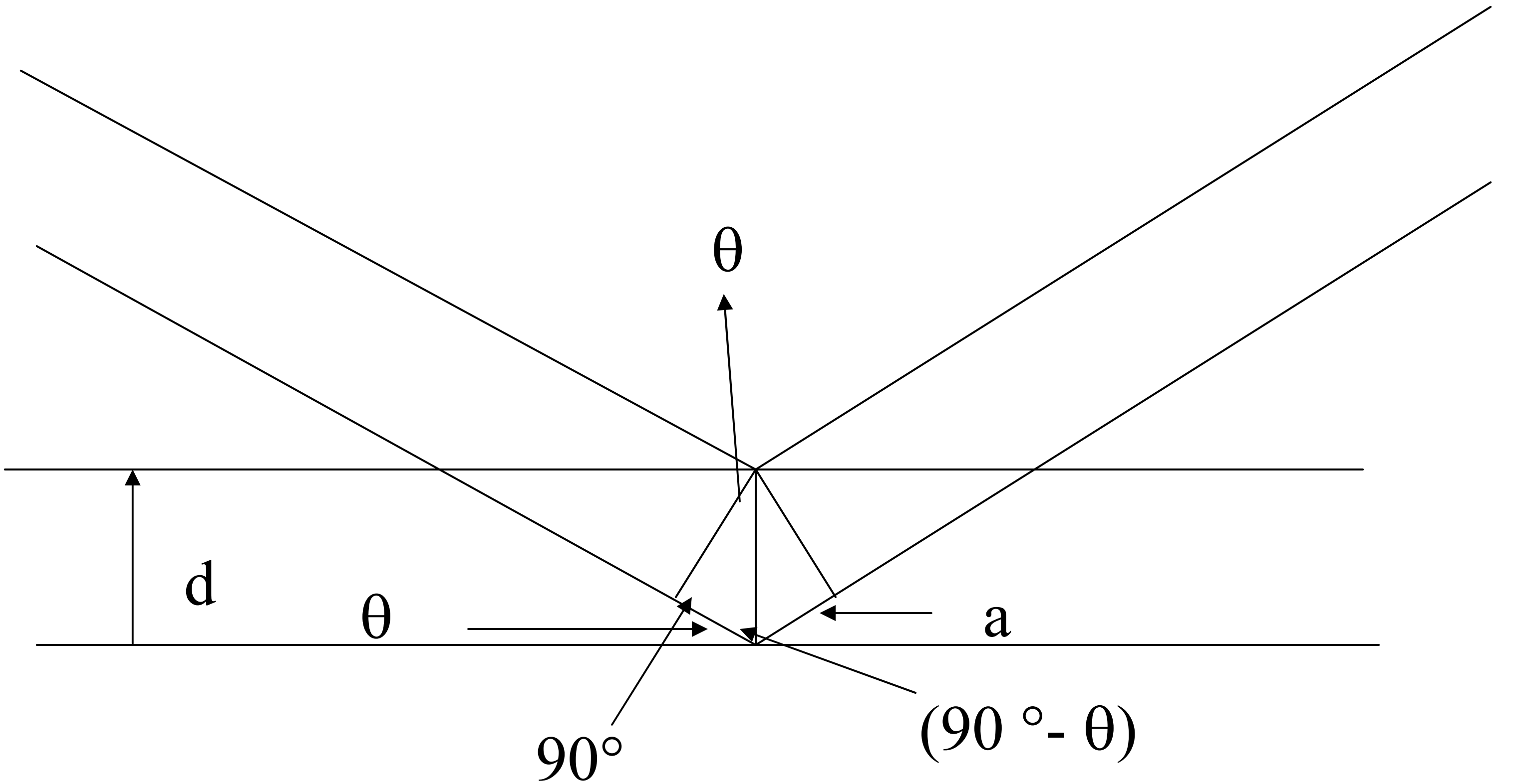


A brief tutorial on some properties of waves, light waves



Incident rays
Reflected rays
λ
θ
A
θ
1st layer of atoms
θ
d
B
B′
2nd layer of atoms
C

λ = wavelength of light

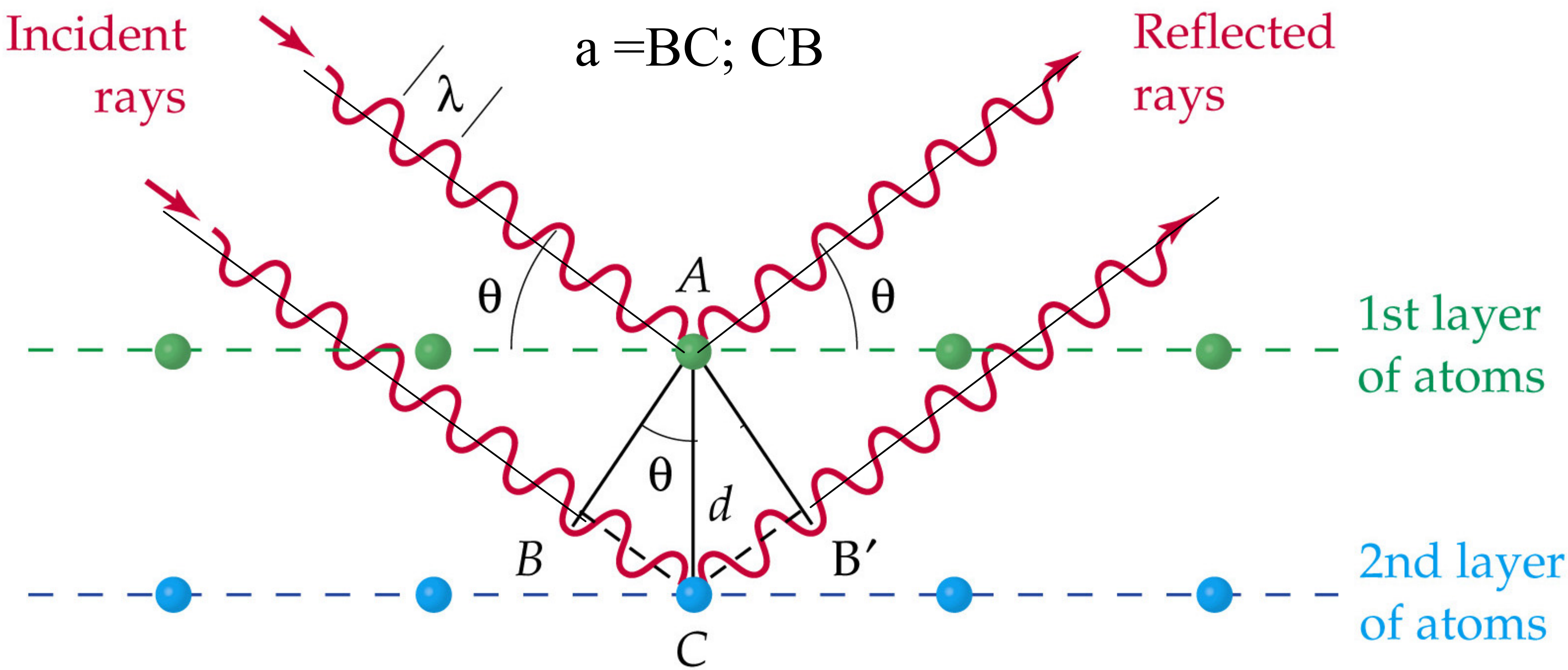


sin θ = a/d

d= a /sin θ or a =dsin θ

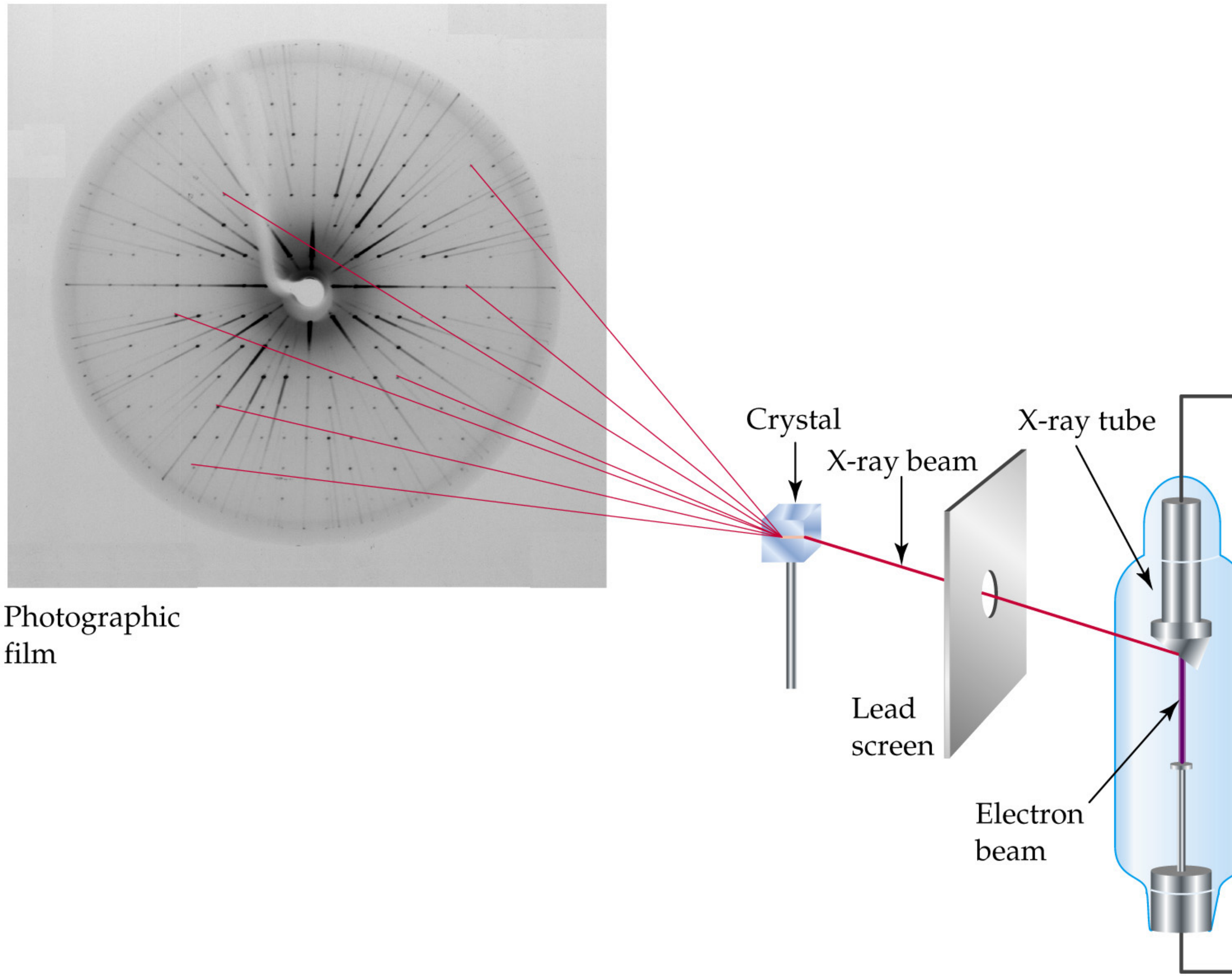
$a = d\sin\theta$

$a = BC; CB$

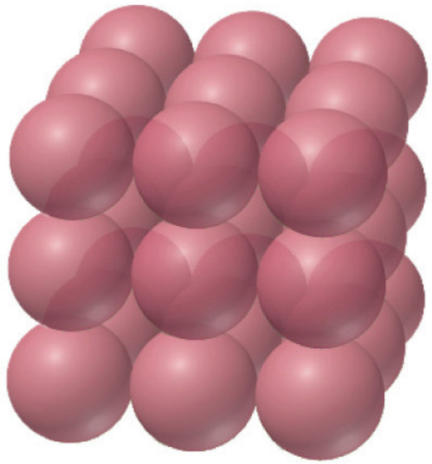


$BC + CB' = 2d\sin\theta = n\lambda$ for constructive interference

$d = n\lambda/2\sin\theta$

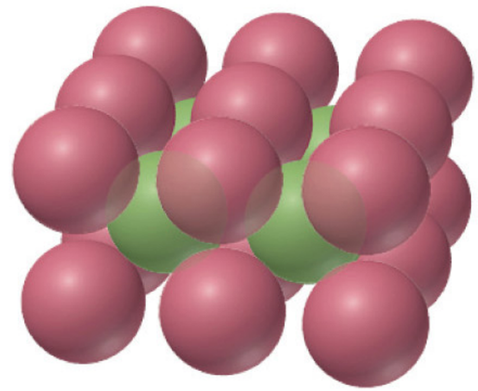

Crystal
X-ray beam
X-ray tube
Photographic film
Lead screen
Electron beam

How do different substances pack in the solid?



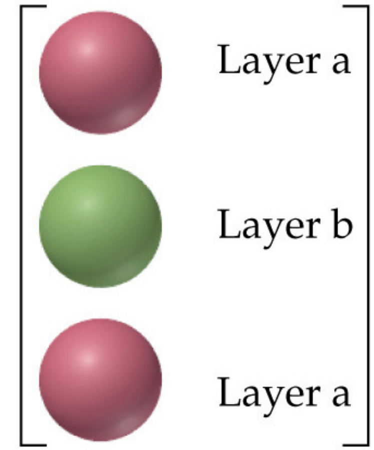
Simple cubic

(a)



Body-centered cubic

(b)



52% of the volume occupied

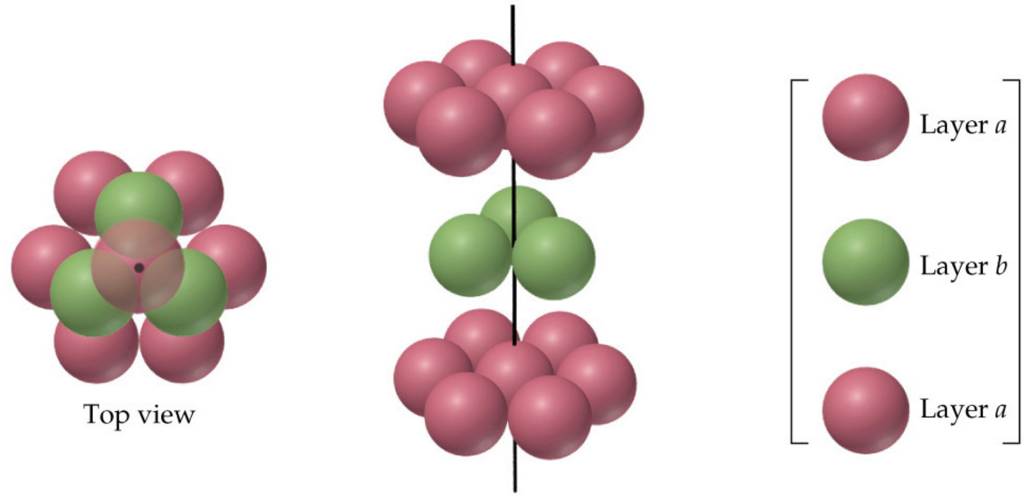
only polonium crystallizes in this motif

68 % of the volume used; examples Fe, Na + 14 other metals

crystallize in this motif

Hexagonal closest packed

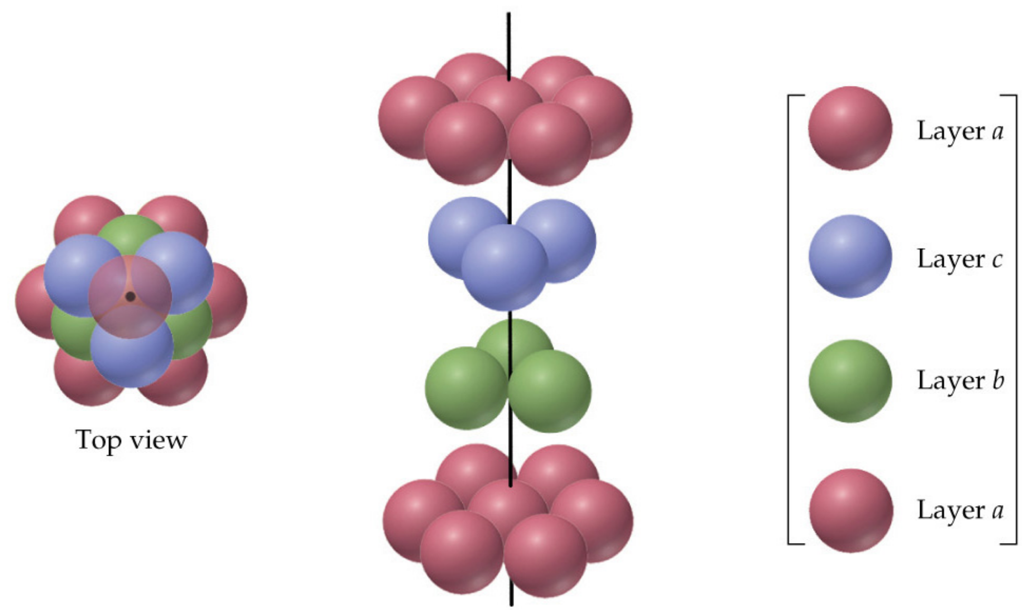
74% of the volume is occupied; Zn, Mg and 19 other metals pack in this motif



(a)

Cubic closest packed

74% of the volume is occupied; Ag, Cu and 16 other metals pack in this motif



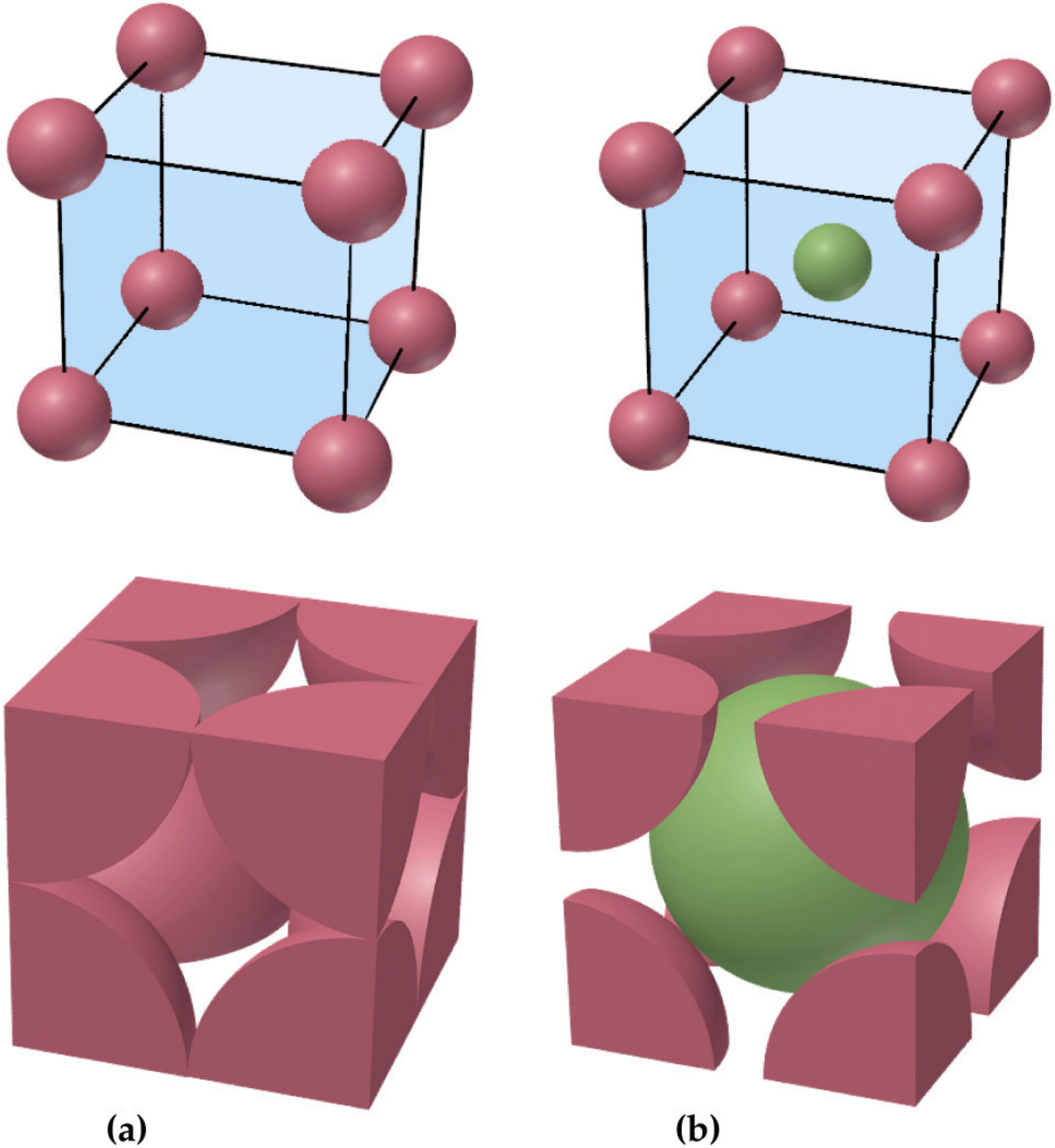
(b)

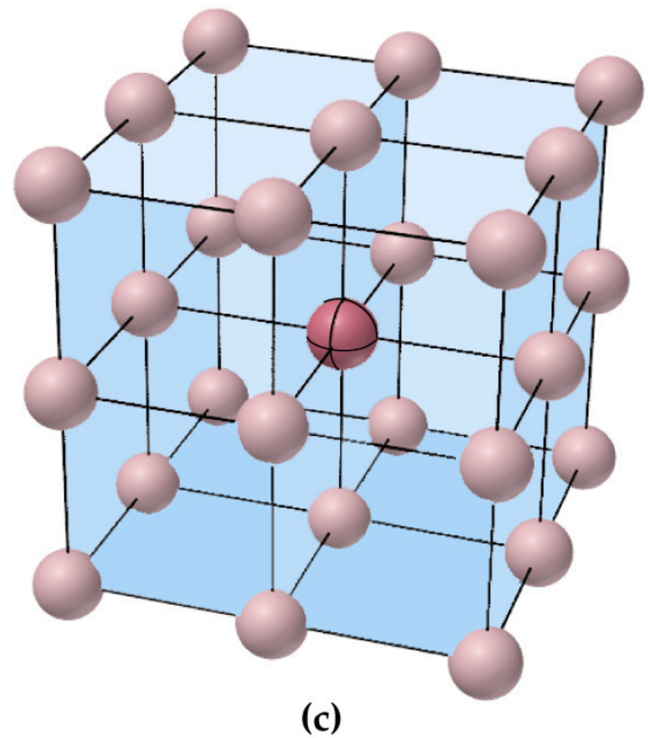
Unit cell: smallest repeat unit that can generate the entire 3-d structure; 14 different unit cell geometries possible

3 different kinds of cubic cell geometry

1. primitive cubic
2. face centered cubic
3. body centered cubic

How many atoms in each of these simplest repeat units?

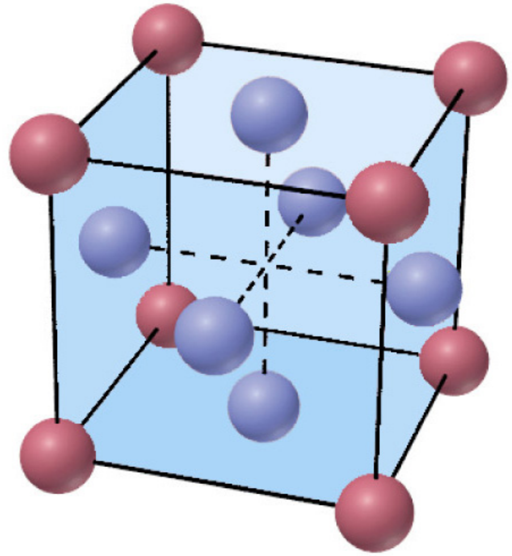




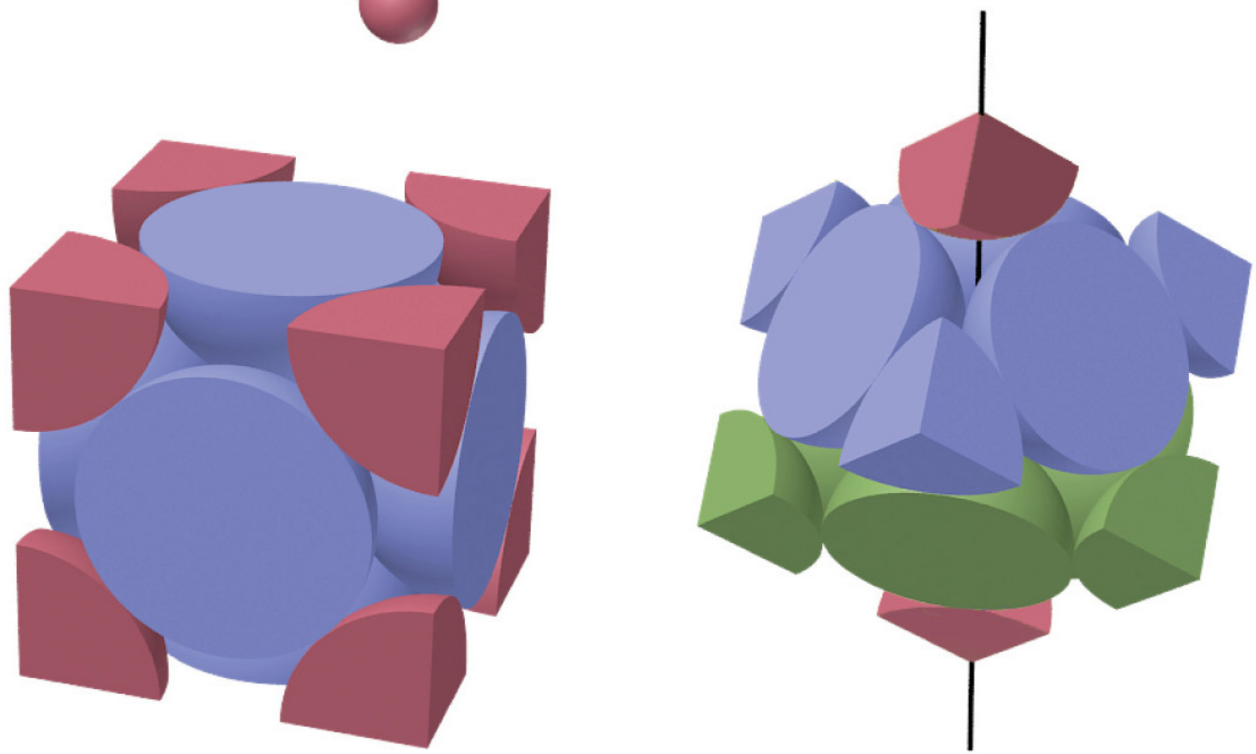
primitive cubic

body centered cubic

Face centered cubic



How many atoms in this unit cell?



(a) (b)

TABLE 10.10 Summary of the Four Kinds of Packing for Spheres

Structure	Stacking Pattern	Coordination Number	Space Used (%)	Unit Cell
Simple cubic	*a-a-a-a-*	6	52	Primitive cubic
Body-centered cubic	*a-b-a-b-*	8	68	Body-centered cubic
Hexagonal closest-packed	*a-b-a-b-*	12	74	(Noncubic)
Cubic closest-packed	*a-b-c-a-b-c-*	12	74	Face-centered cubic

Copper crystallizes in a face centered cubic unit cell with an edge length of 3.62×10^{-8} cm.

How many atoms in a unit cell of Cu? 4

What is the radius of a copper atom and what is the density of Cu?

$h^2 = edge^2 + edge^2$

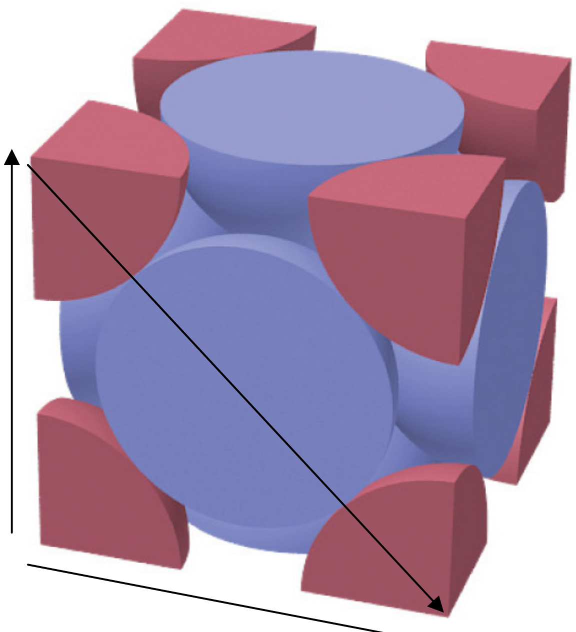
$h^2 = 2*(3.62 \times 10^{-8})^2$

$h = [26.2 \times 10^{-16}]^{1/2}$

$h = 5.12 \times 10^{-8}$ cm

How many radui is h?

4, radius = 1.28×10^{-8} cm



Volume of unit cell? $V = r^3$

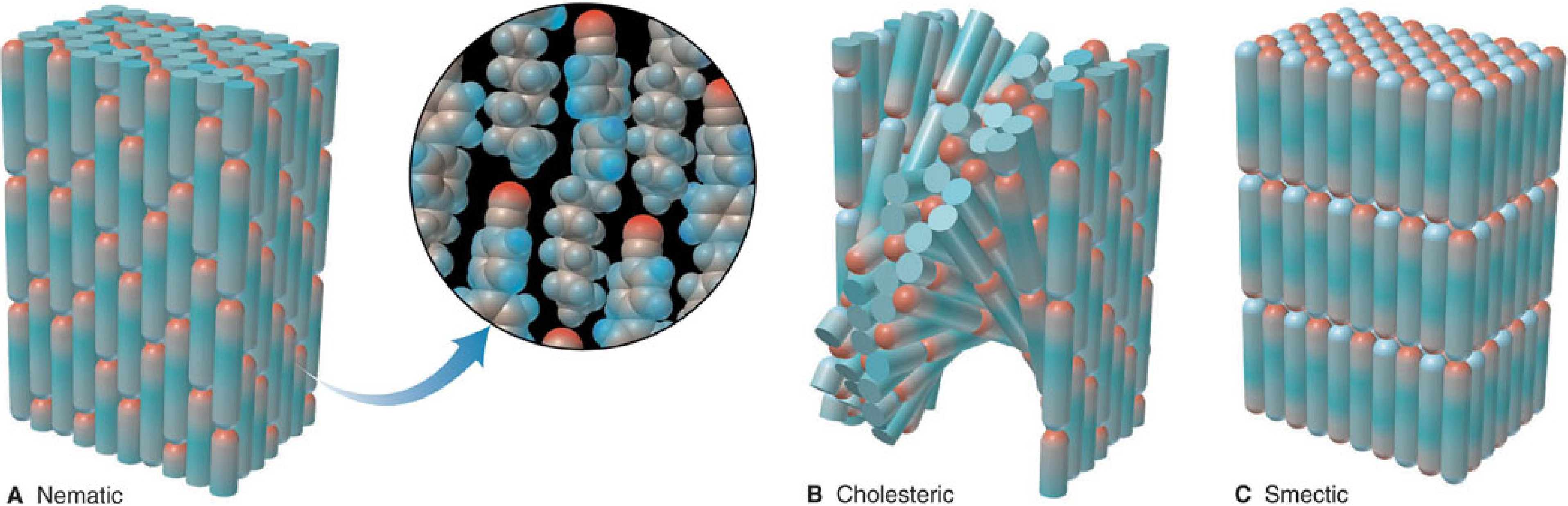
$V = (3.62 \times 10^{-8})^3 = 47.8 \times 10^{-24}$ cm^3

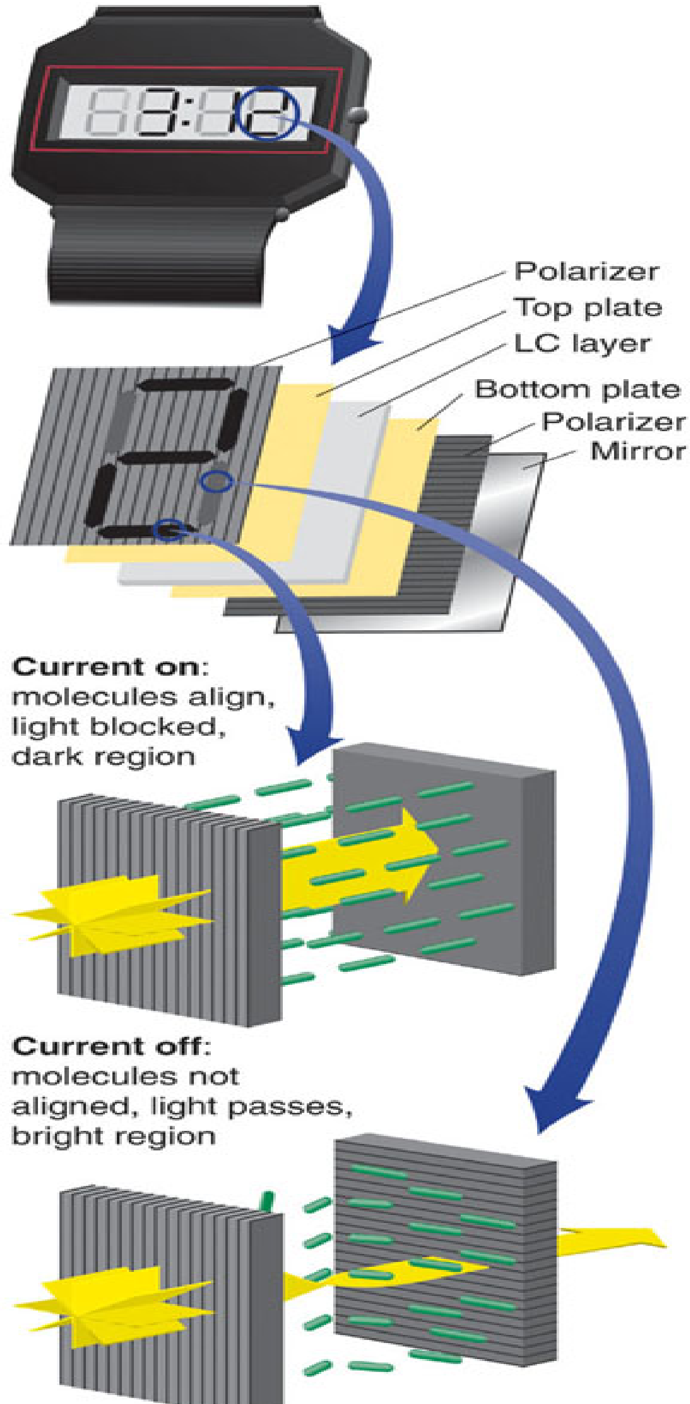
How many atoms? 4 atoms

If 4 atoms have this volume, then 6×10^{23} atoms would have a volume of $6 \times 10^{23} \times 47.8 \times 10^{-24}/4$ cm^3 = 7.17 cm^3

63.5g/7.17cm^3 = 8.85 g/cm^3 ; 8.94g/cm^3 (25 °C)

Liquid Crystals




Polarizer
Top plate
LC layer
Bottom plate
Polarizer
Mirror
Current on: molecules align, light blocked, dark region
Current off: molecules not aligned, light passes, bright region