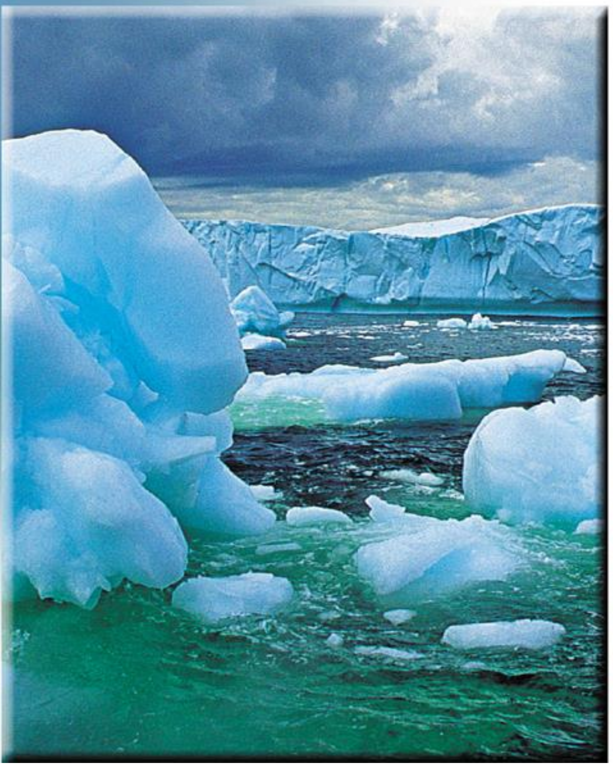
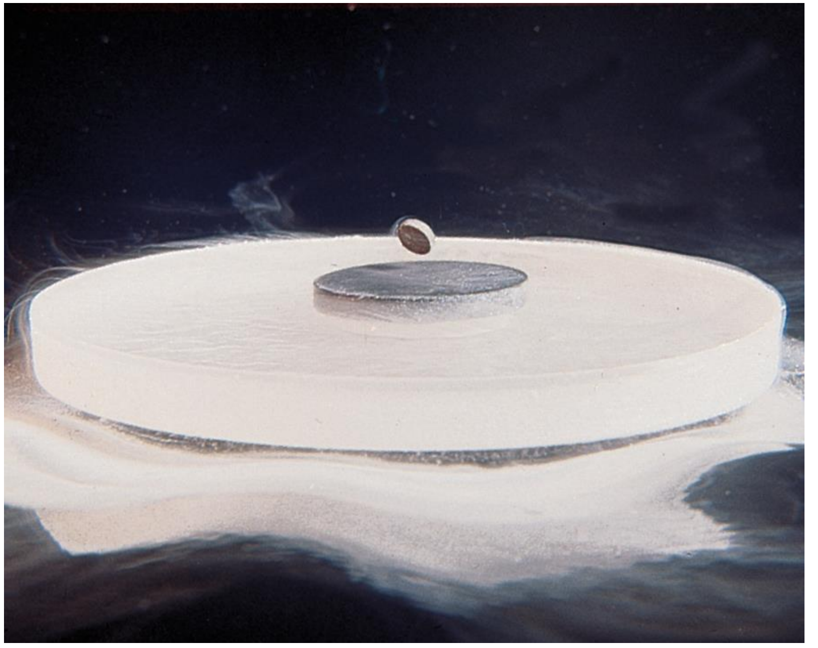
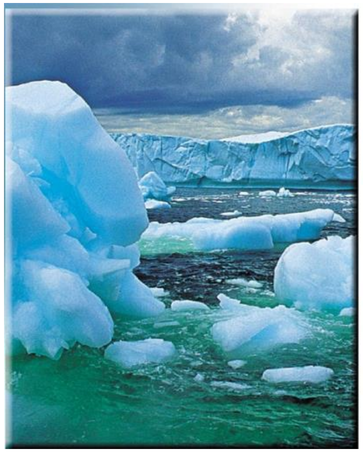




Intermolecular Forces and Liquids and Solids

Chapter 11

A ***phase*** is a homogeneous part of the system in contact with other parts of the system but separated from them by a well-defined boundary.



<u>2 Phases</u>

Solid phase - ice

Liquid phase - water

Table 12.1 **Characteristic Properties of Gases, Liquids, and Solids**

State of Matter	Volume/Shape	Density	Compressibility	Motion of Molecules
Gas	Assumes the volume and shape of its container	Low	Very compressible	Very free motion
Liquid	Has a definite volume but assumes the shape of its container	High	Only slightly compressible	Slide past one another freely
Solid	Has a definite volume and shape	High	Virtually incompressible	Vibrate about fixed positions

Intermolecular Forces

Intermolecular forces are attractive forces **between** molecules.

Intramolecular forces hold atoms together in a molecule.

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**)

Generally, **inter**molecular forces are much weaker than **intra**molecular forces.

"Measure" of intermolecular force

boiling point

melting point

ΔH_{vap}

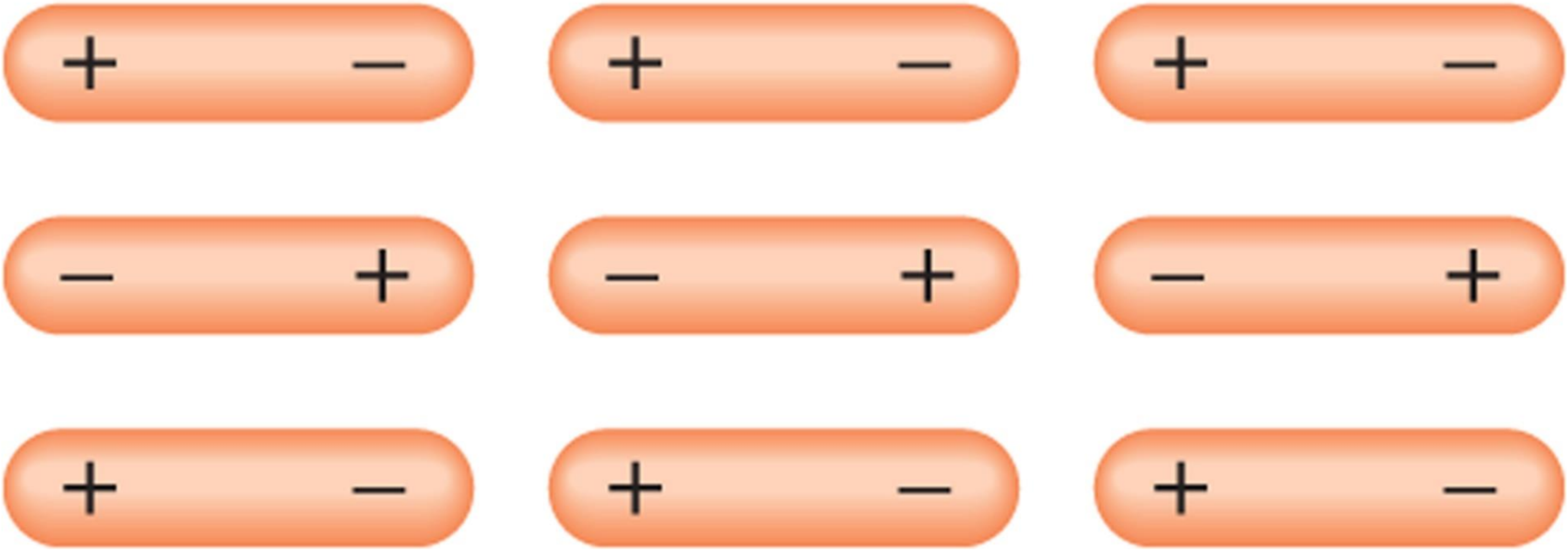
ΔH_{fus}

ΔH_{sub}

Intermolecular Forces

Dipole-Dipole Forces

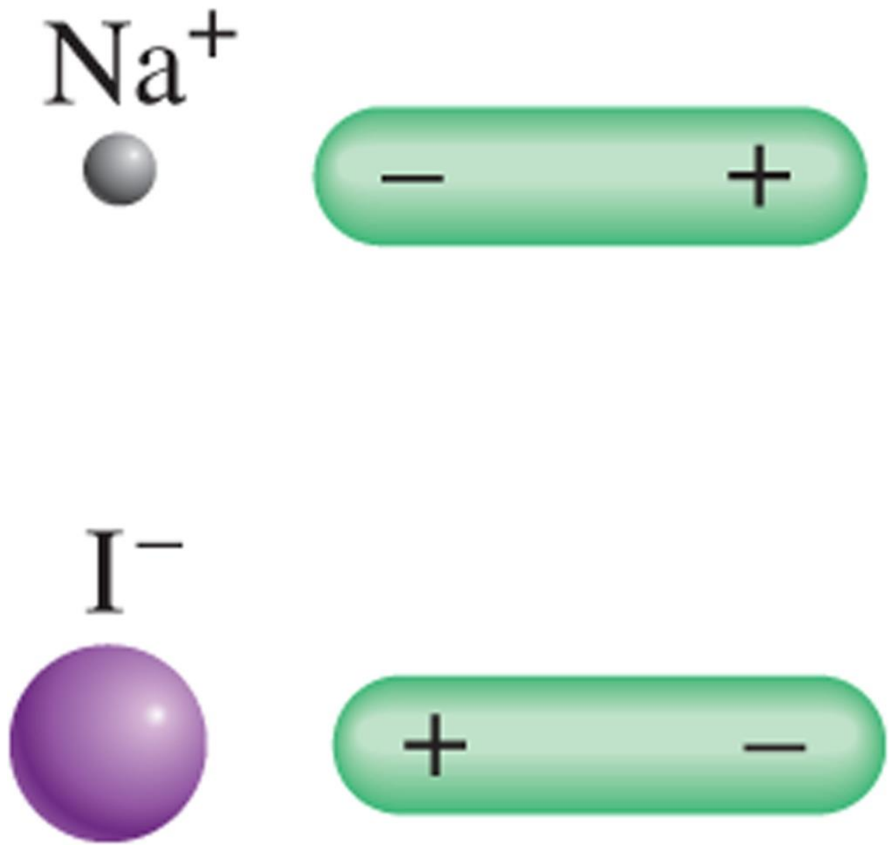
Attractive forces between **polar molecules**



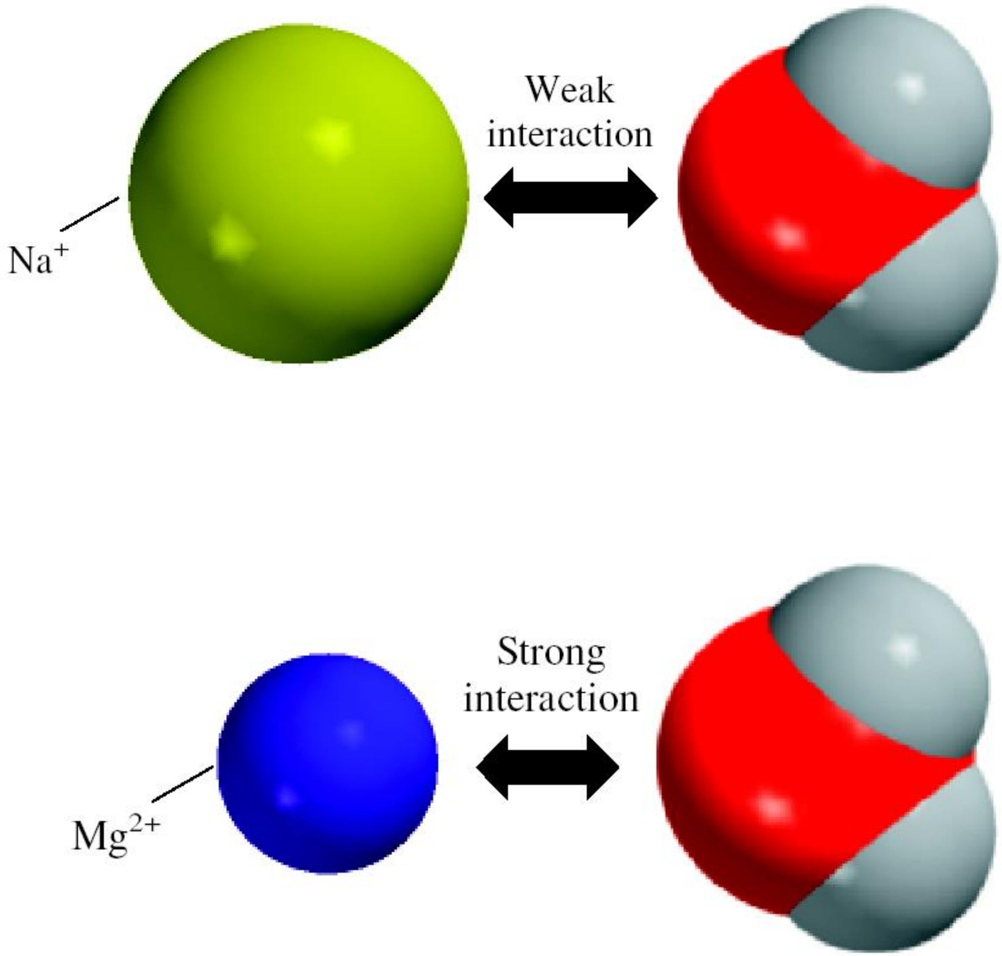
Intermolecular Forces

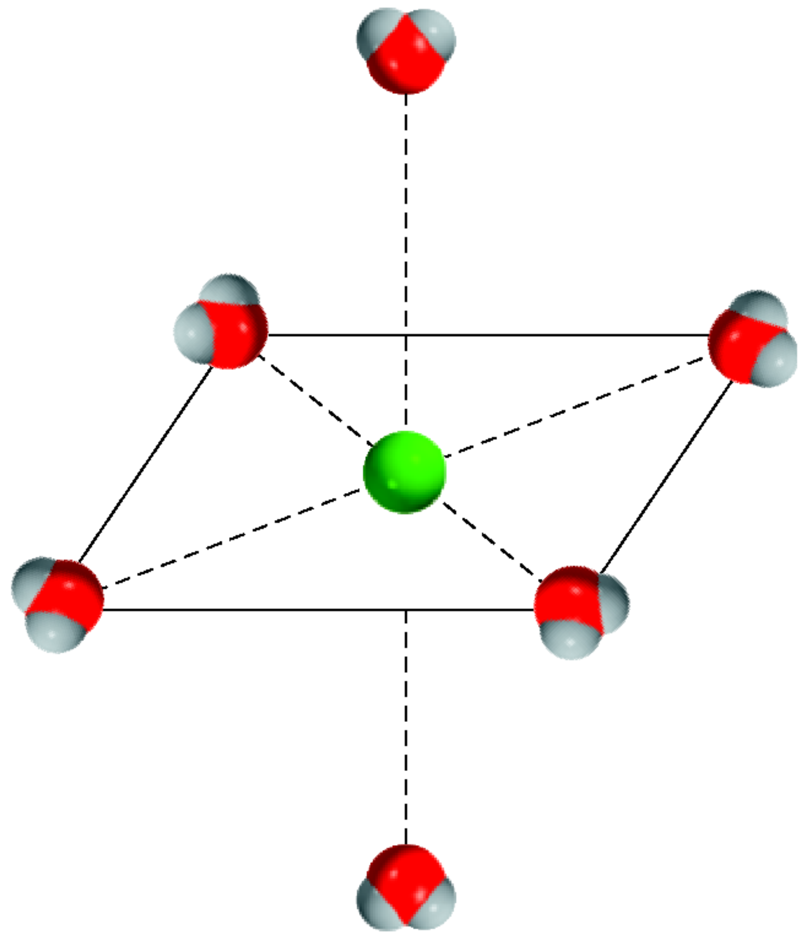
Ion-Dipole Forces

Attractive forces between an **ion** and a **polar molecule**



Interaction Between Water and Cations



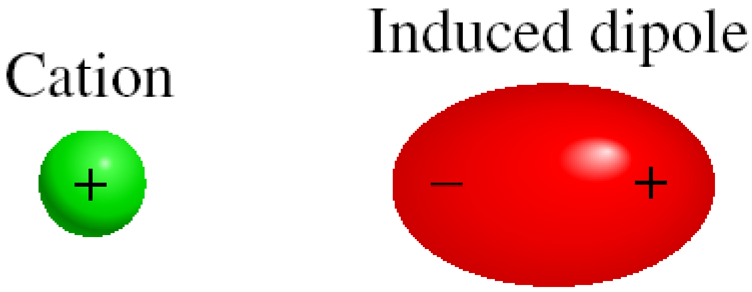


in solution

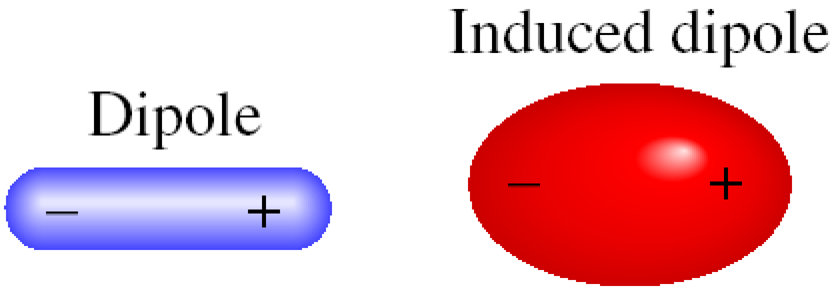
Intermolecular Forces

Dispersion Forces

Attractive forces that arise as a result of **temporary dipoles induced** in atoms or molecules

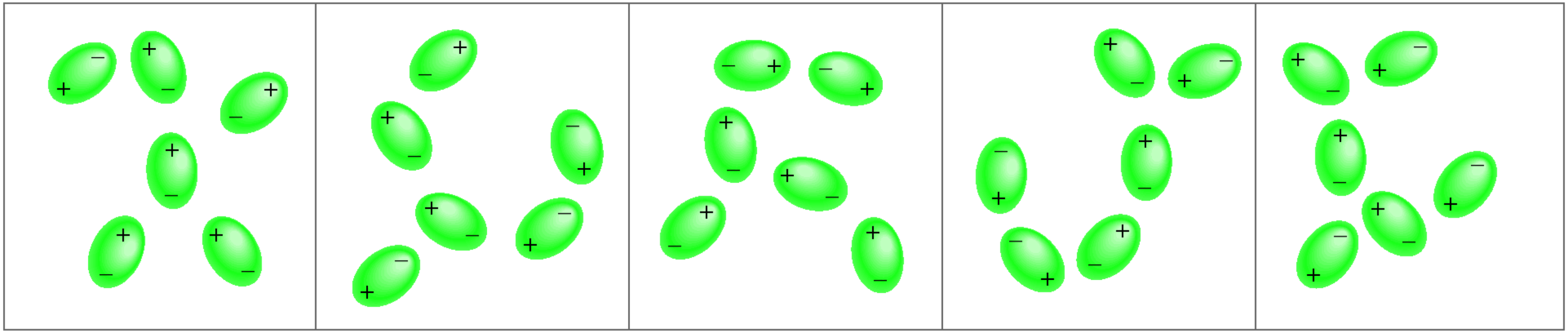


ion-induced dipole interaction



dipole-induced dipole interaction

Induced Dipoles Interacting With Each Other



Dispersion Forces Continued

Polarizability is the ease with which the electron distribution in the atom or molecule can be distorted.

Polarizability increases with:

- greater number of electrons
- more diffuse electron cloud

Dispersion forces usually increase with molar mass.

Table 12.2

Melting Points of Similar Nonpolar Compounds

Compound	Melting Point (°C)
CH_4	−182.5
CF_4	−150.0
CCl_4	−23.0
CBr_4	90.0
CI_4	171.0

Example 12.1

What type(s) of intermolecular forces exist between the following pairs?

(a) HBr and H_2S

(b) Cl_2 and CBr_4

(c) I_2 and NO_3^-

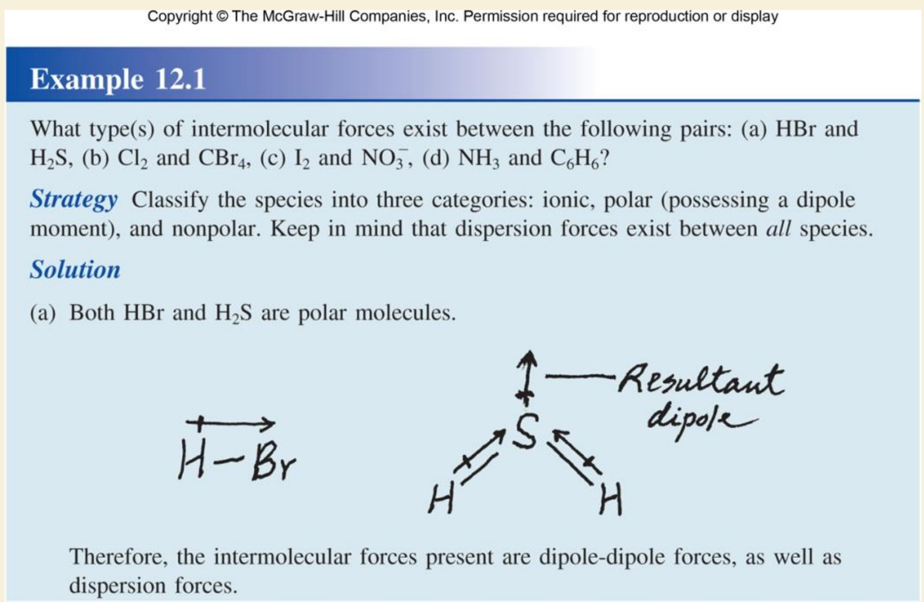
(d) NH_3 and C_6H_6

Example 12.1

Strategy Classify the species into three categories: ionic, polar (possessing a dipole moment), and nonpolar. Keep in mind that dispersion forces exist between *all* species.

Solution

(a) Both HBr and H_2S are polar molecules. Therefore, the intermolecular forces present are dipole-dipole forces, as well as dispersion forces.



Example 12.1

What type(s) of intermolecular forces exist between the following pairs: (a) HBr and H_2S, (b) Cl_2 and CBr_4, (c) I_2 and NO_3^-, (d) NH_3 and C_6H_6?

Strategy Classify the species into three categories: ionic, polar (possessing a dipole moment), and nonpolar. Keep in mind that dispersion forces exist between *all* species.

Solution

(a) Both HBr and H_2S are polar molecules.

Therefore, the intermolecular forces present are dipole-dipole forces, as well as dispersion forces.

Example 12.1

(b) Both Cl_2 and CBr_4 are nonpolar, so there are only dispersion forces between these molecules.

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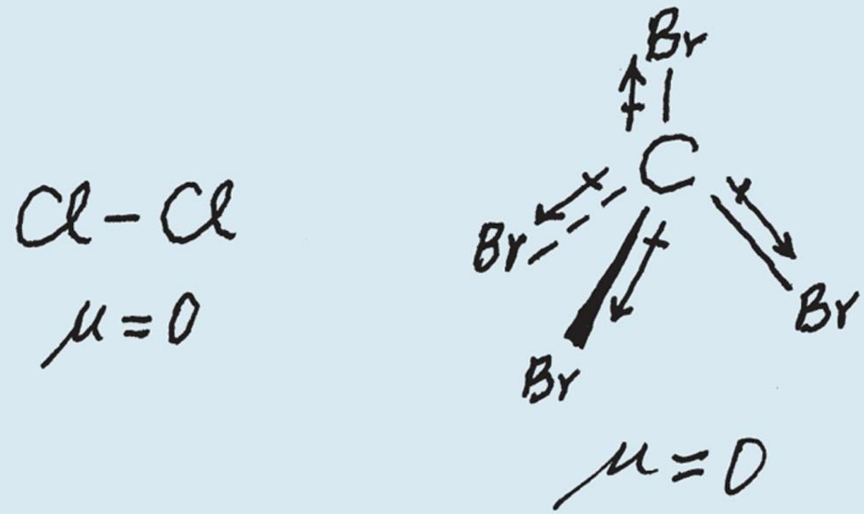


(c) I_2 is a homonuclear diatomic molecule and therefore nonpolar, so the forces between it and the ion NO_3^- are ion-induced dipole forces and dispersion forces.

(d) NH_3 is polar, and C_6H_6 is nonpolar. The forces are dipole-induced dipole forces and dispersion forces.

Practice Exercise Name the type(s) of intermolecular forces that exists between molecules (or basic units) in each of the following species: (a) LiF, (b) CH_4, (c) SO_2.

Example 12.1

(c) I_2 is a homonuclear diatomic molecule and therefore nonpolar, so the forces between it and the ion NO_3^- are ion-induced dipole forces and dispersion forces.

(d) NH_3 is polar, and C_6H_6 is nonpolar. The forces are dipole-induced dipole forces and dispersion forces.

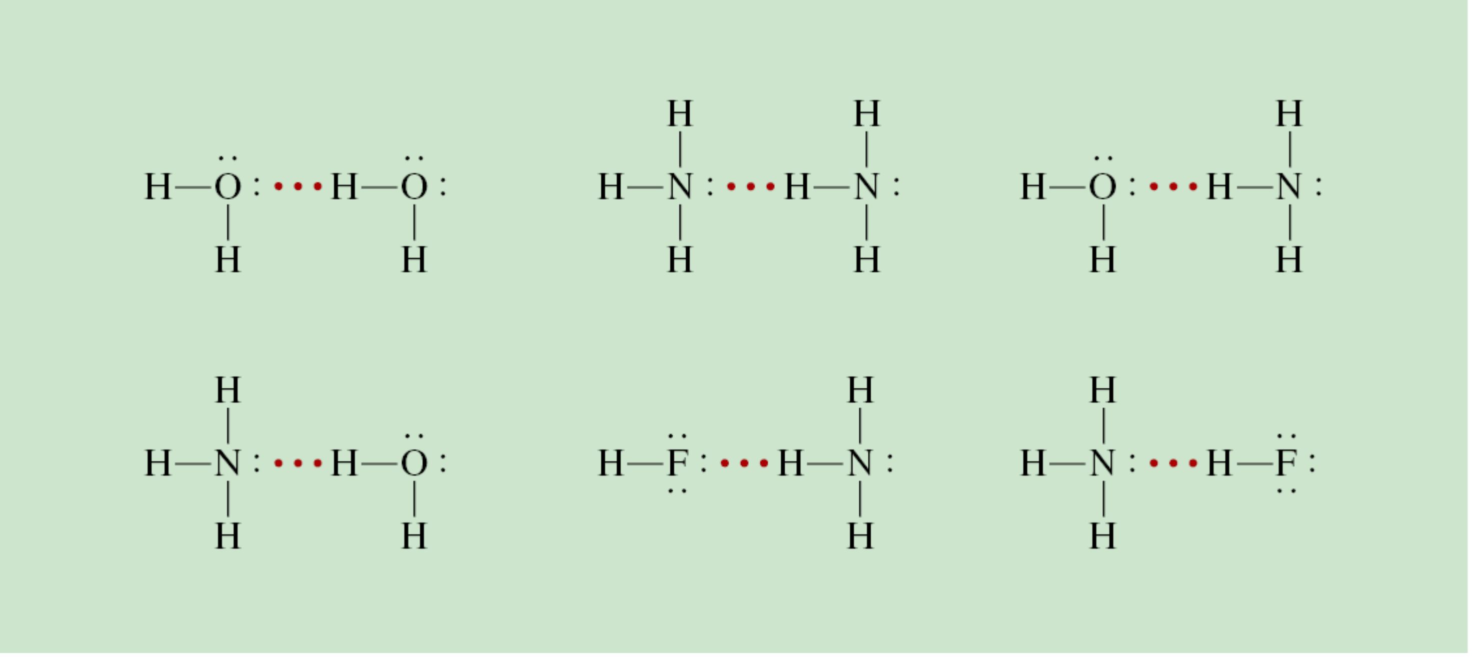
Intermolecular Forces

Hydrogen Bond

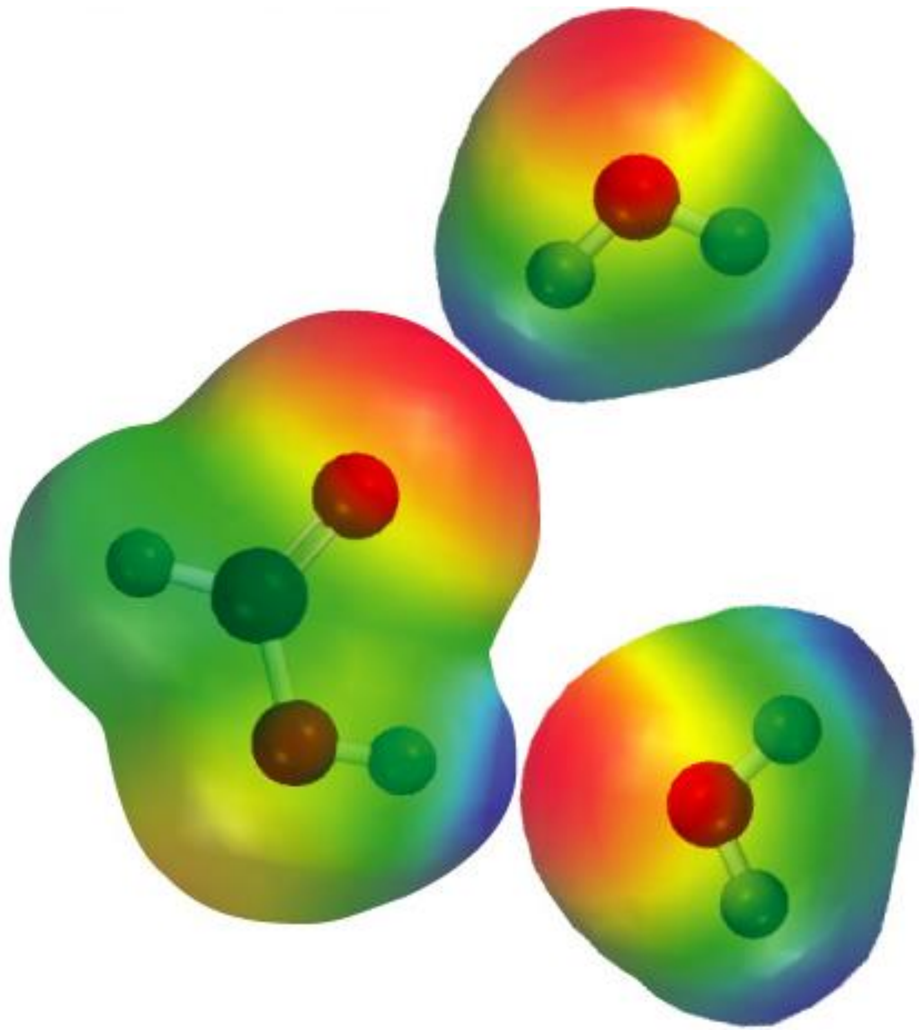
The ***hydrogen bond*** is a special dipole-dipole interaction between the hydrogen atom in a polar N-H, O-H, or F-H bond and an electronegative O, N, or F atom.

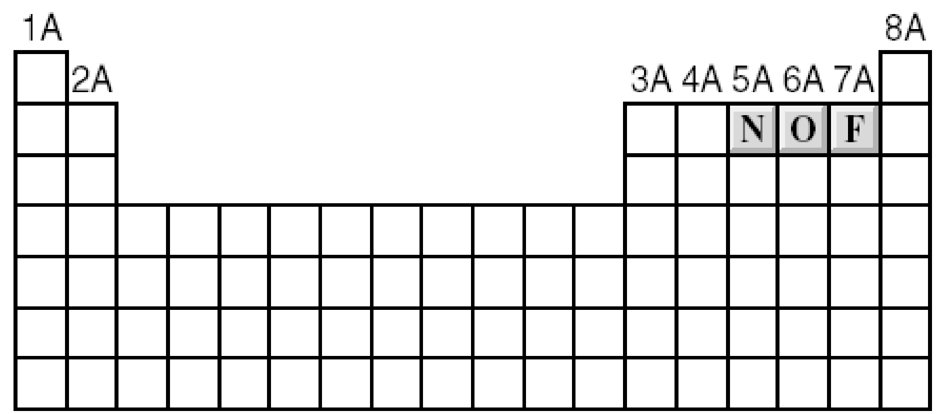
$$A - H \cdots B \quad \text{or} \quad A - H \cdots A$$

A & B are N, O, or F



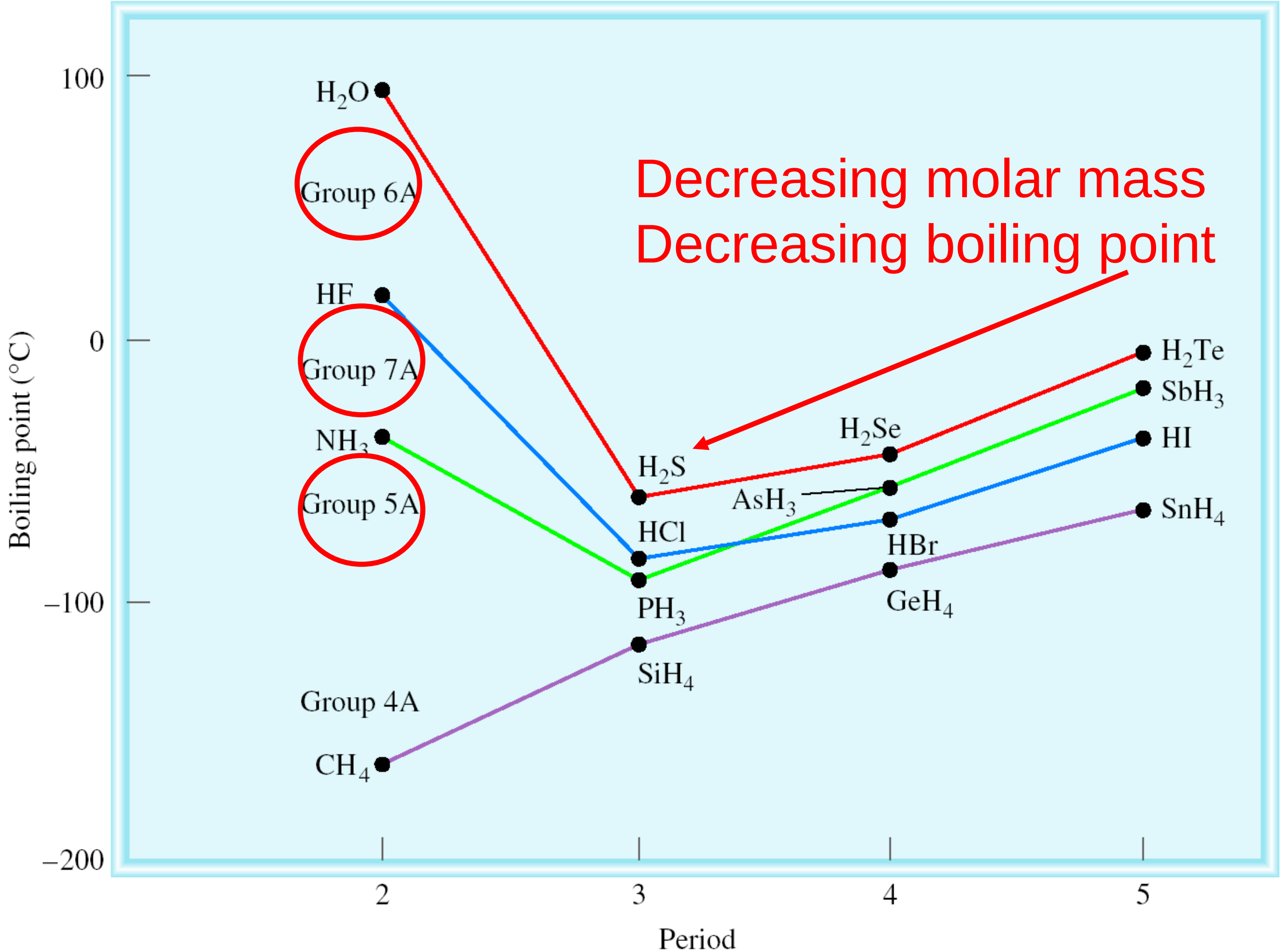
Hydrogen Bond





HCOOH and water

Why is the hydrogen bond considered a "special" dipole-dipole interaction?



Example 12.2

Which of the following can form hydrogen bonds with water?

CH_3OCH_3

CH_4

F^-

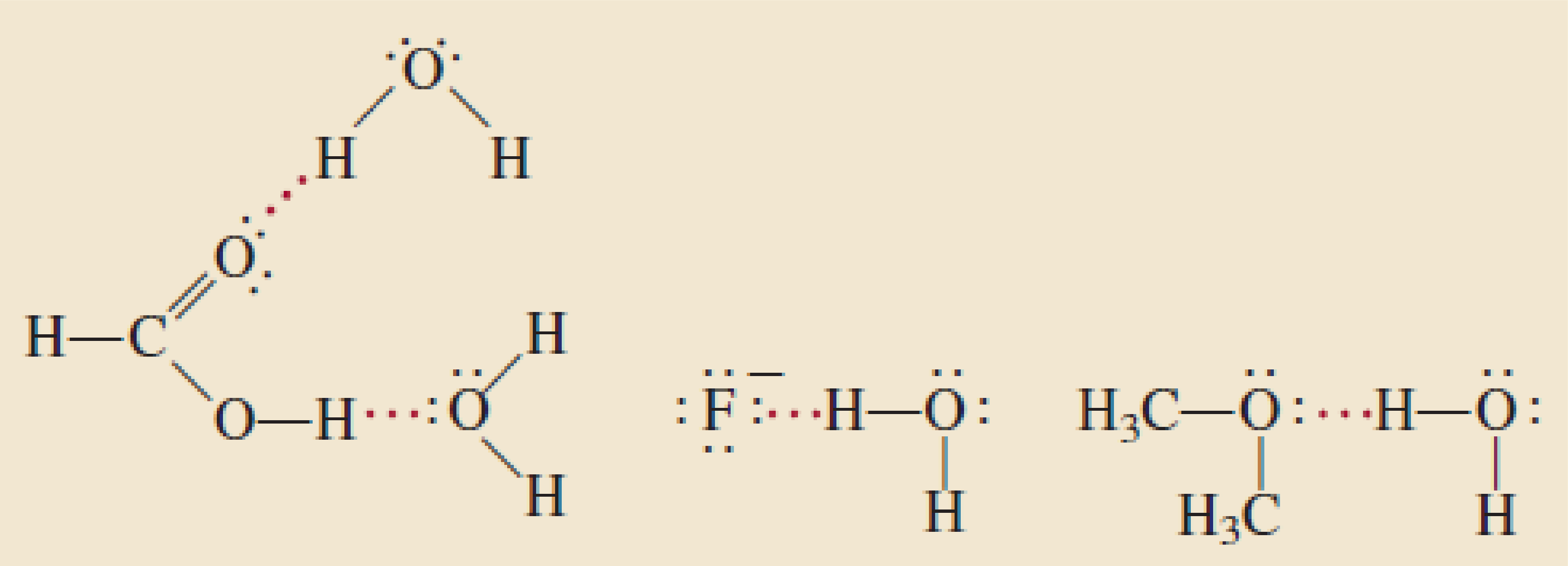
$HCOOH$

Na^+

Example 12.2

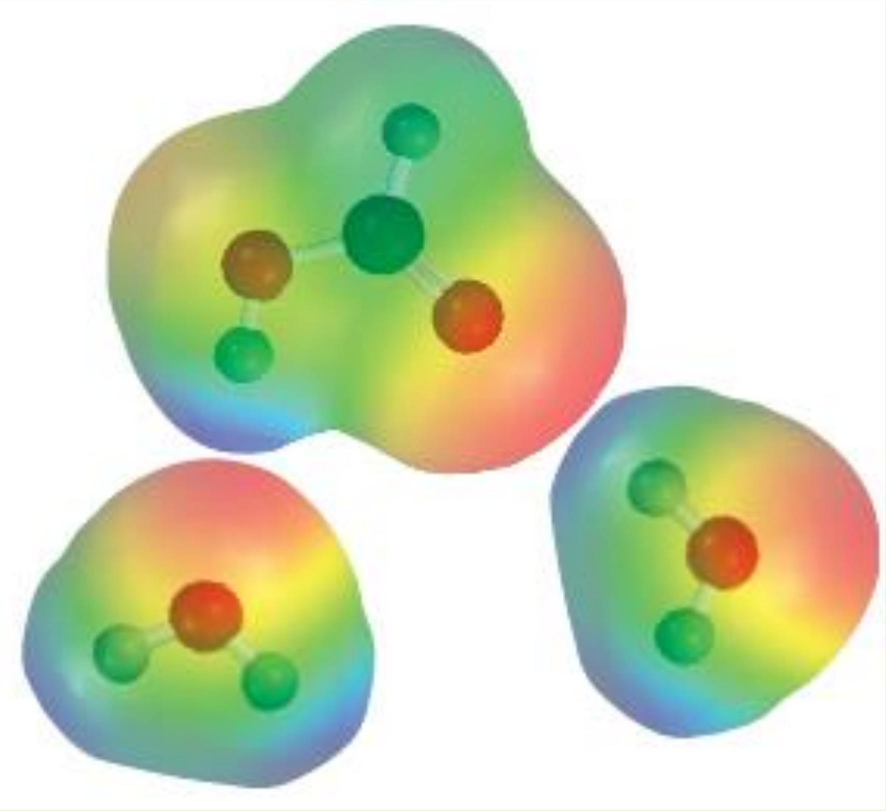
Strategy A species can form hydrogen bonds with water if it contains one of the three electronegative elements (F, O, or N) or it has a H atom bonded to one of these three elements.

Solution There are no electronegative elements (F, O, or N) in either CH_4 or Na^+. Therefore, only CH_3OCH_3, F^-, and HCOOH can form hydrogen bonds with water.



Example 12.2

Check Note that HCOOH (formic acid) can form hydrogen bonds with water in two different ways.



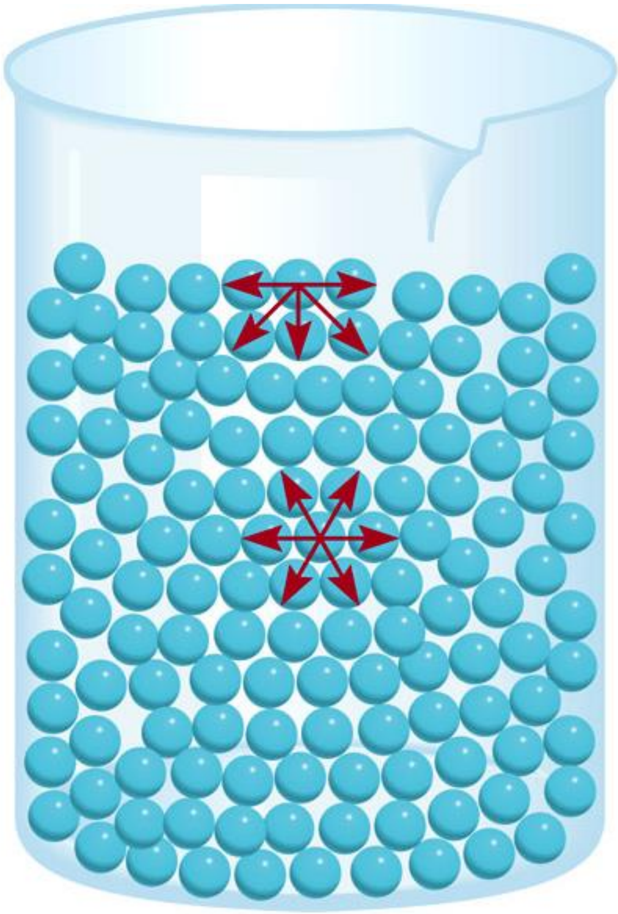
HCOOH forms hydrogen bonds
with two H_2O molecules.

Properties of Liquids

Surface tension is the amount of energy required to stretch or increase the surface of a liquid by a unit area.

Strong intermolecular forces

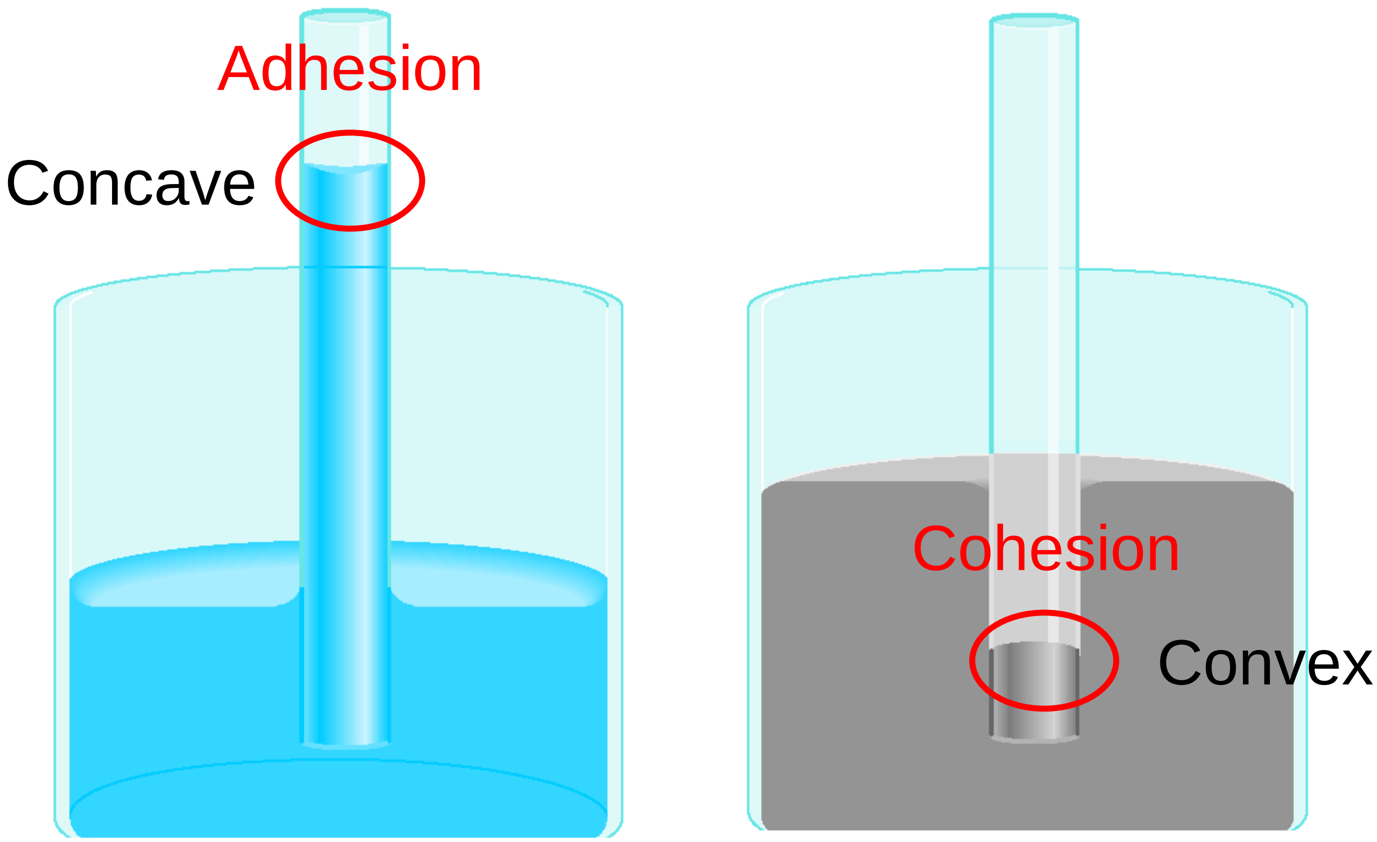
High surface tension



Properties of Liquids

Cohesion is the intermolecular attraction between like molecules

Adhesion is an attraction between unlike molecules



Adh > Coh

Coh >Adh

Properties of Liquids

Viscosity is a measure of a fluid's resistance to flow.

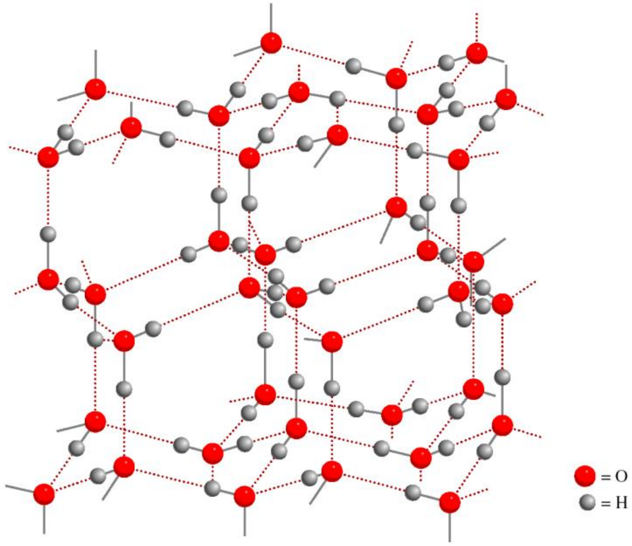
Strong intermolecular forces

High viscosity

Table 12.3 Viscosity of Some Common Liquids at 20°C

Liquid	Viscosity (N s/m^2)*
Acetone (C_3H_6O)	3.16×10^{-4}
Benzene (C_6H_6)	6.25×10^{-4}
Blood	4×10^{-3}
Carbon tetrachloride (CCl_4)	9.69×10^{-4}
Diethyl ether ($C_2H_5OC_2H_5$)	2.33×10^{-4}
Ethanol (C_2H_5OH)	1.20×10^{-3}
Glycerol ($C_3H_8O_3$)	1.49
Mercury (Hg)	1.55×10^{-3}
Water (H_2O)	1.01×10^{-3}

3-D Structure of Water

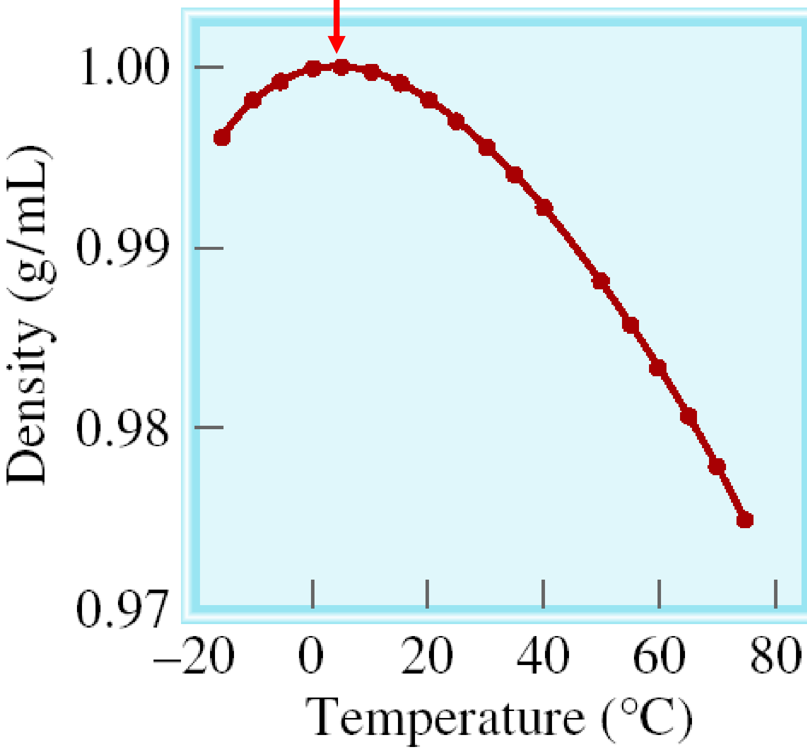


Ice is less dense than water

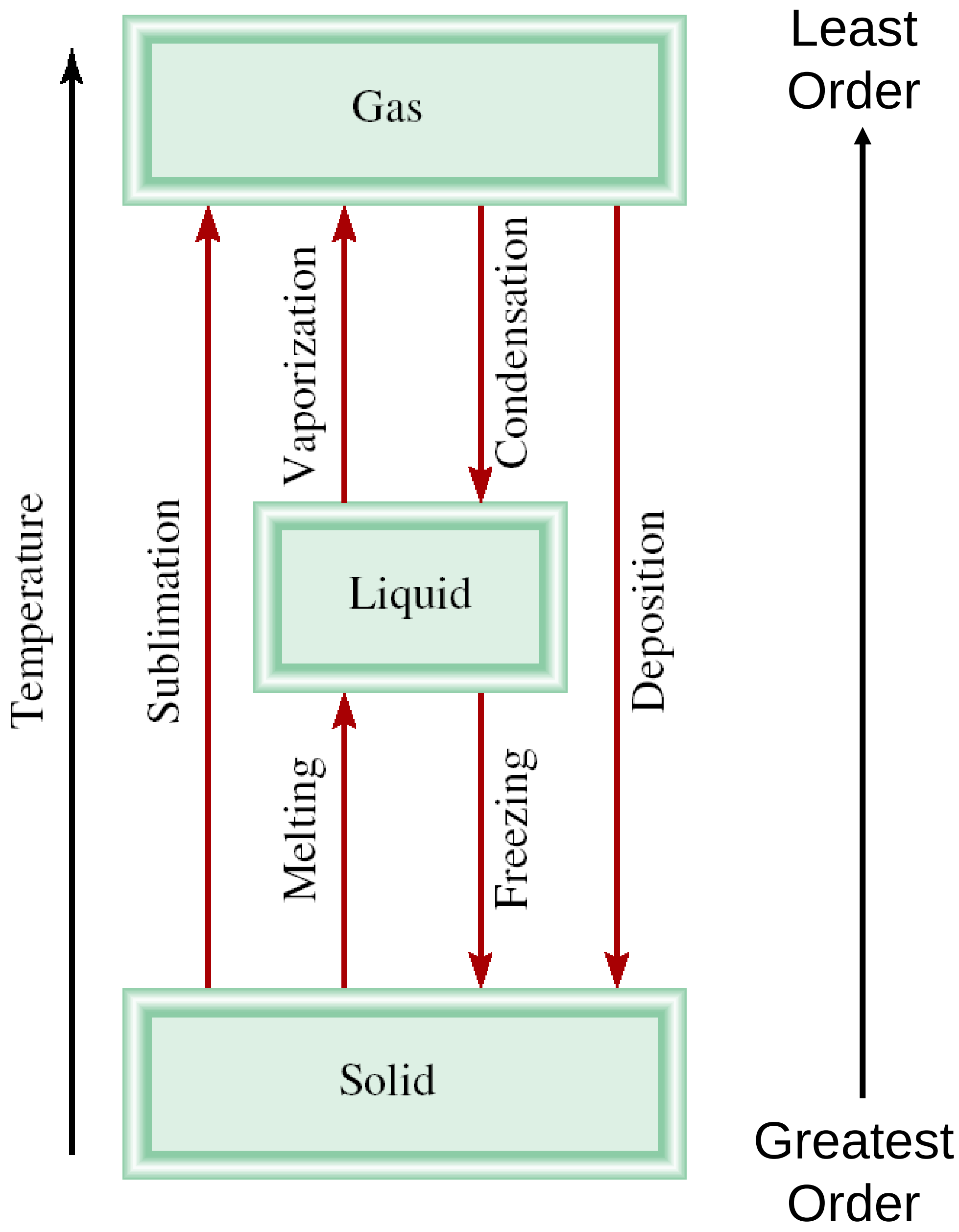
Water is a Unique Substance

Maximum Density
4^0C

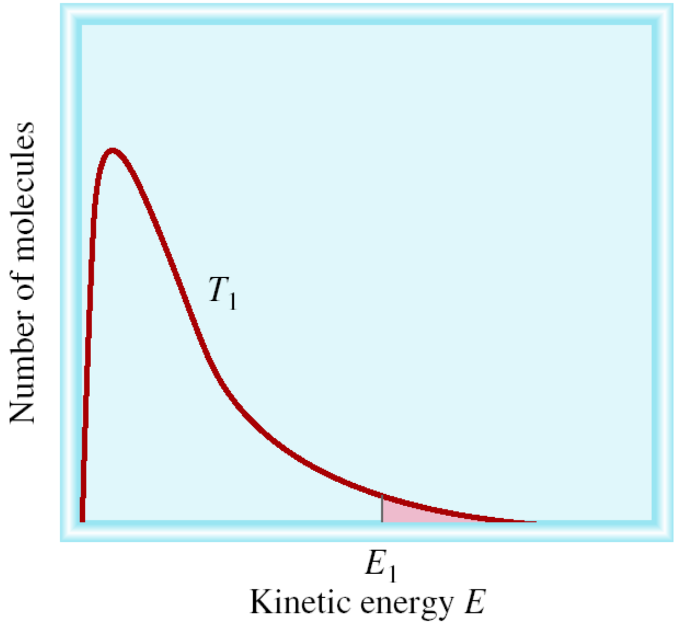
Density of Water



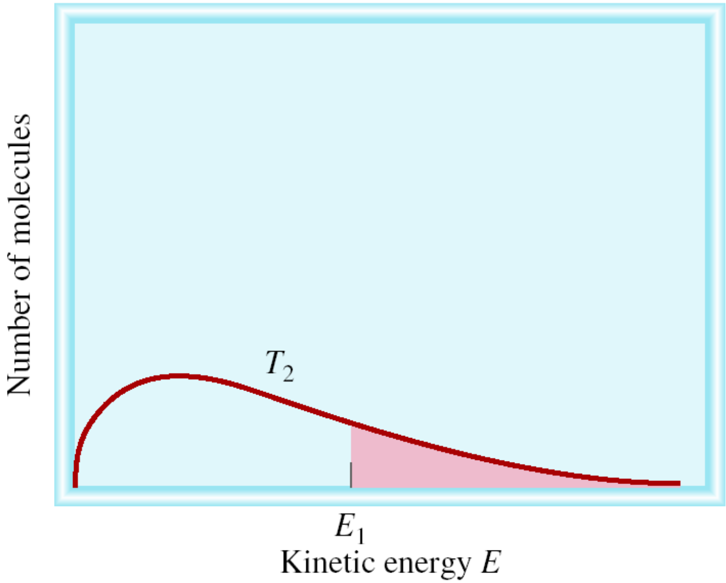
Phase Changes



Effect of Temperature on Kinetic Energy



$T_2 > T_1$

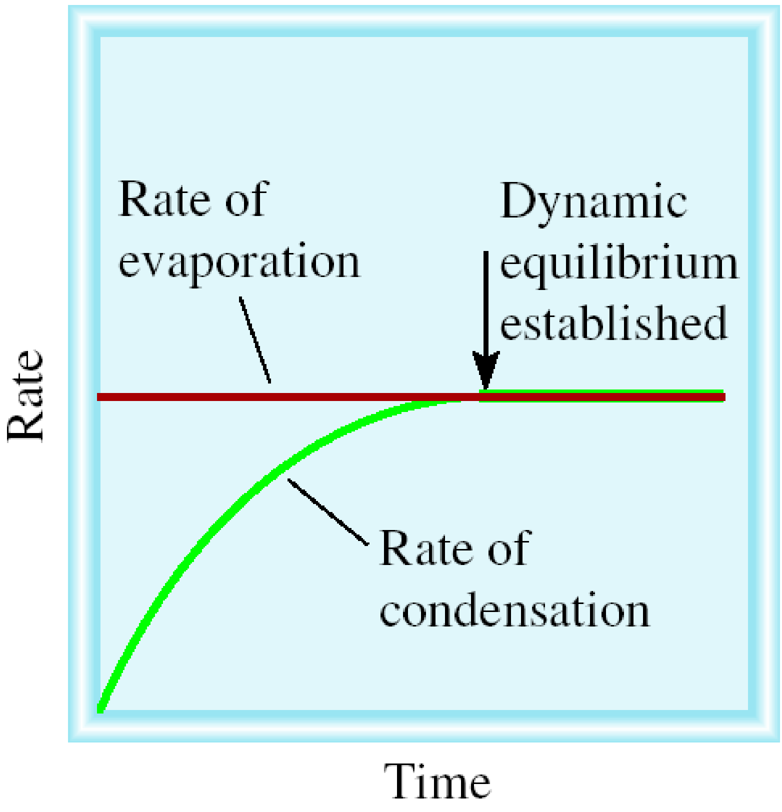


The ***equilibrium vapor pressure*** is the vapor pressure measured when a dynamic equilibrium exists between condensation and evaporation

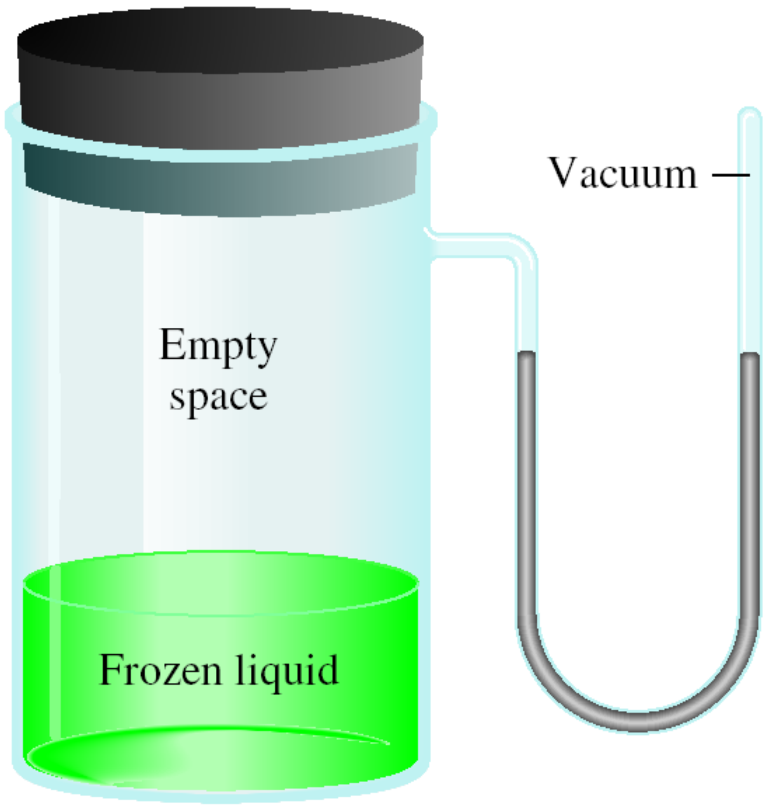
$$H_2O\ (l) \rightleftharpoons H_2O\ (g)$$

Dynamic Equilibrium

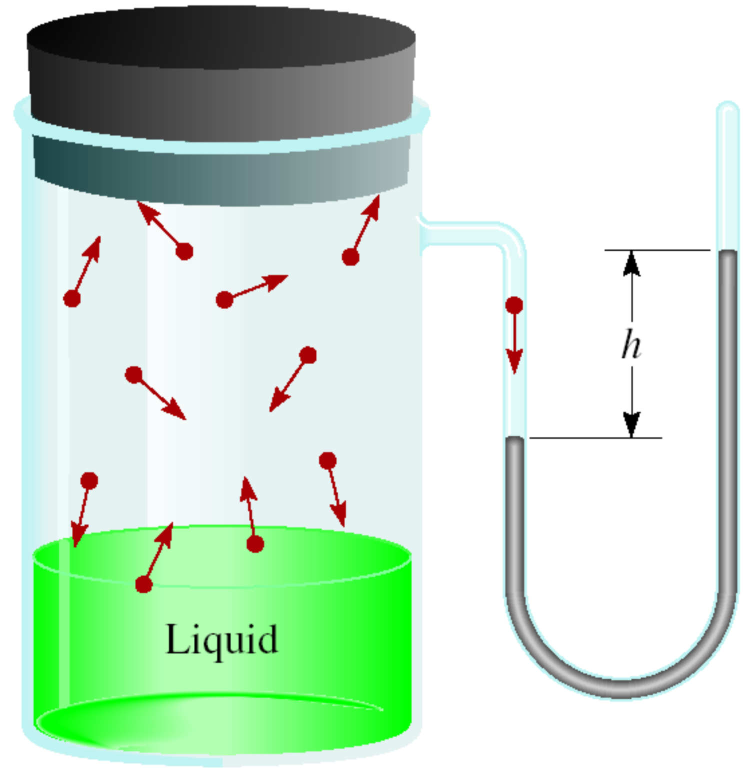
Rate of condensation = Rate of evaporation



Measurement of Vapor Pressure



Before Evaporation



At Equilibrium

Molar heat of vaporization (ΔH_{vap}) is the energy required to vaporize 1 mole of a liquid at its boiling point.

Clausius-Clapeyron Equation

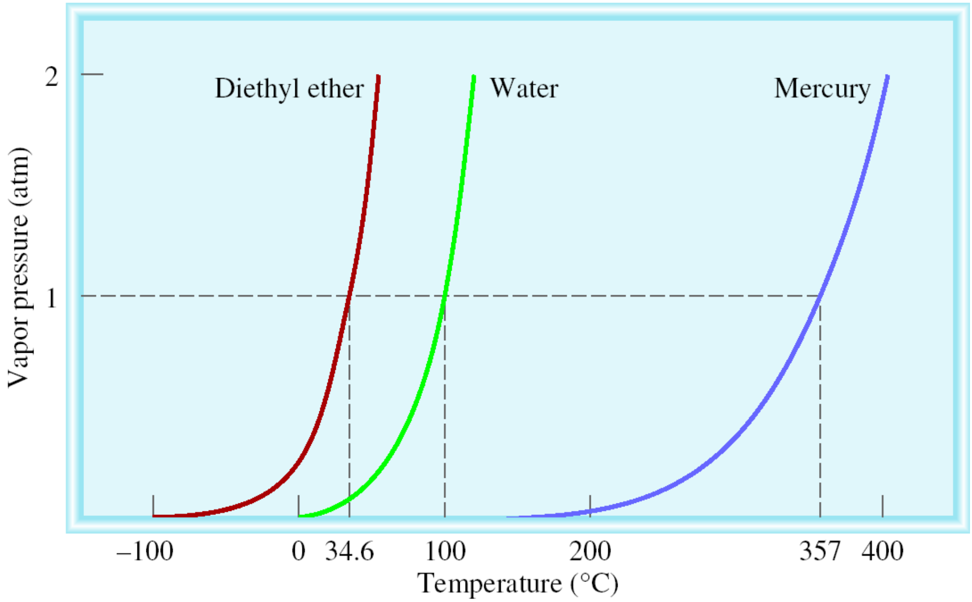
$$\ln P = -\frac{\Delta H_{vap}}{RT} + C$$

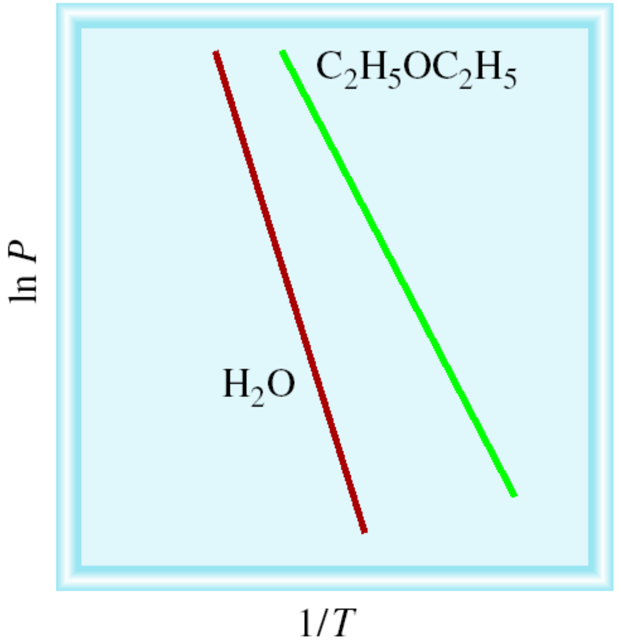
P = (equilibrium) vapor pressure

T = temperature (K)

R = gas constant (8.314 J/K•mol)

Vapor Pressure Versus Temperature





Alternate Forms of the Clausius-Clapeyron Equation

At two temperatures

$$\ln \frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

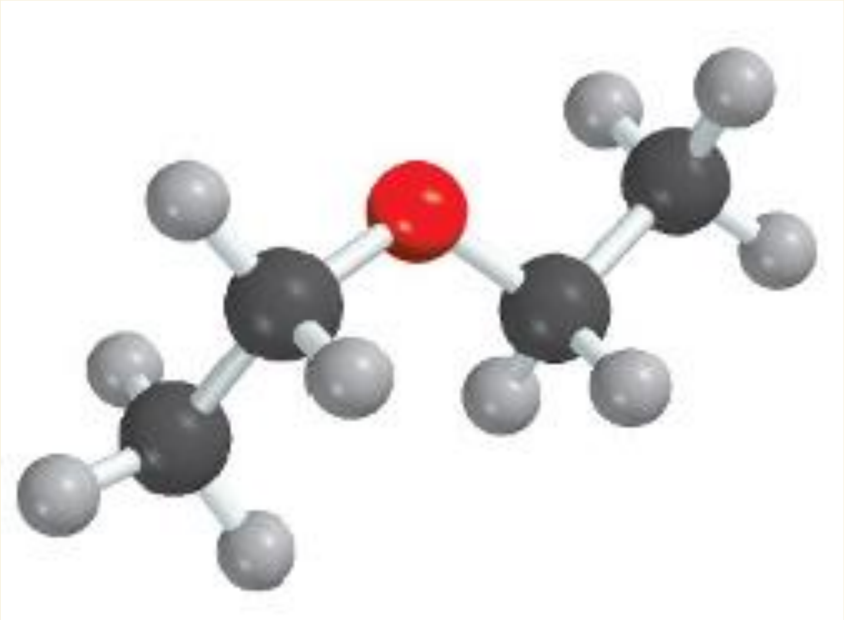
or

$$\ln \frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

Example 12.5

Diethyl ether is a volatile, highly flammable organic liquid that is used mainly as a solvent.

The vapor pressure of diethyl ether is 401 mmHg at 18°C. Calculate its vapor pressure at 32°C.



Example 12.5

Strategy We are given the vapor pressure of diethyl ether at one temperature and asked to find the pressure at another temperature. Therefore, we need Equation (12.4).

Solution Table 12.5 tells us that ΔH_{vap} = 26.0 kJ/mol. The data are

$$P_1 = 401 \text{ mmHg} \qquad P_2 = ?$$
$$T_1 = 18°\text{C} = 291 \text{ K} \qquad T_2 = 32°\text{C} = 305 \text{ K}$$

From Equation (12.4) we have

$$\ln \frac{401}{P_2} = \frac{26{,}000 \text{ J/mol}}{8.314 \text{ J/K} \cdot \text{mol}} \left[\frac{291 \text{ K} - 305 \text{ K}}{(291 \text{ K})(305 \text{ K})} \right]$$
$$= -0.493$$

Example 12.5

Taking the antilog of both sides (see Appendix 3), we obtain

$$\frac{401}{P_2} = e^{-0.493} = 0.611$$

Hence

$$P_2 = 656 \text{ mmHg}$$

Check We expect the vapor pressure to be greater at the higher temperature. Therefore, the answer is reasonable.

The ***boiling point*** is the temperature at which the (equilibrium) vapor pressure of a liquid is equal to the external pressure.

The ***normal boiling point*** is the temperature at which a liquid boils when the external pressure is 1 atm.

Table 12.5 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
Diethyl ether ($C_2H_5OC_2H_5$)	34.6	26.0
Ethanol (C_2H_5OH)	78.3	39.3
Mercury (Hg)	357	59.0
Methane (CH_4)	−164	9.2
Water (H_2O)	100	40.79

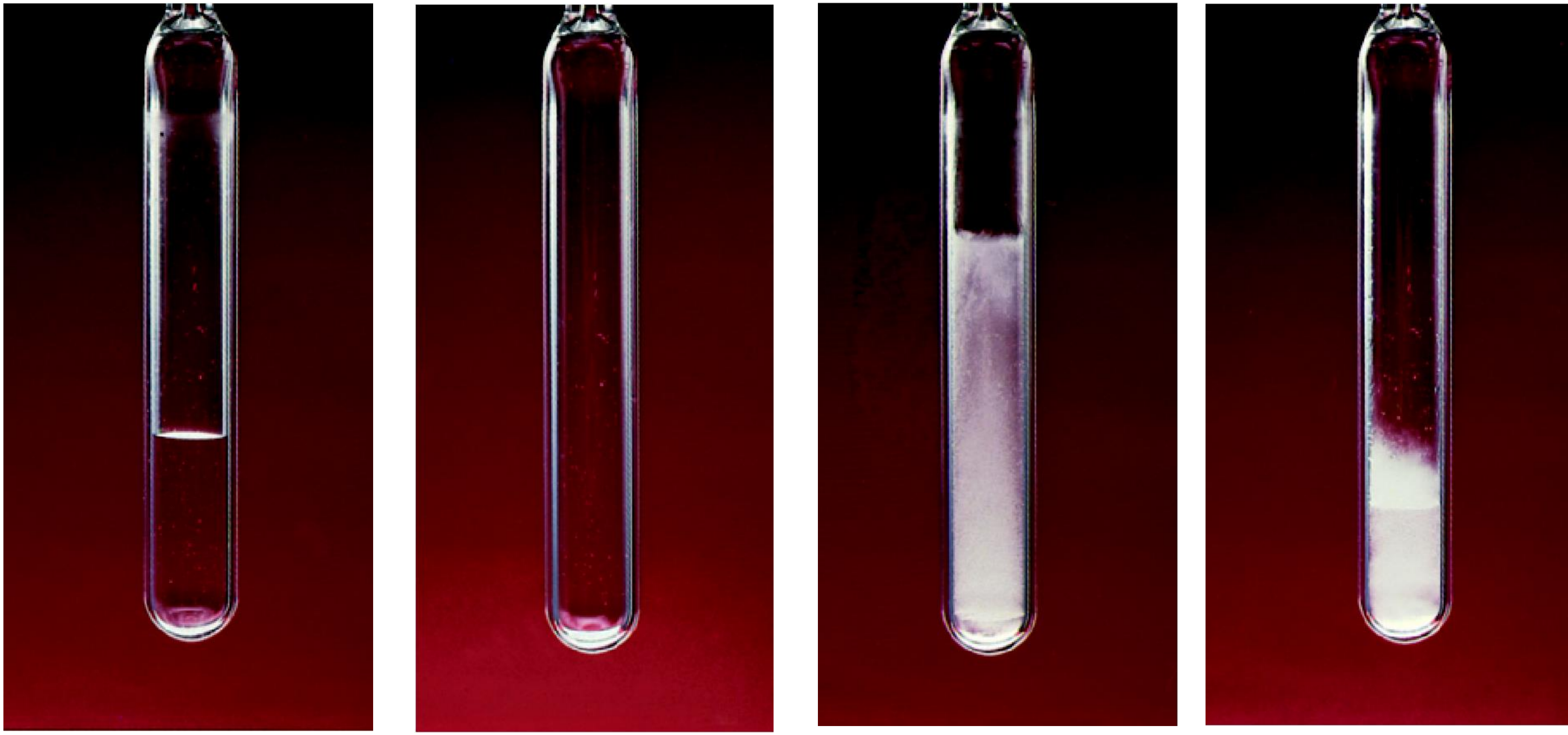
The ***critical temperature*** (***T_c***) is the temperature above which the gas cannot be made to liquefy, no matter how great the applied pressure.

The ***critical pressure*** (***P_c***) is the minimum pressure that must be applied to bring about liquefaction at the critical temperature.

Table 12.6 Critical Temperatures and Critical Pressures of Selected Substances

Substance	T_c(°C)	P_c(atm)
Ammonia (NH_3)	132.4	111.5
Argon (Ar)	−186	6.3
Benzene (C_6H_6)	288.9	47.9
Carbon dioxide (CO_2)	31.0	73.0
Diethyl ether ($C_2H_5OC_2H_5$)	192.6	35.6
Ethanol (C_2H_5OH)	243	63.0
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

The Critical Phenomenon of SF_6

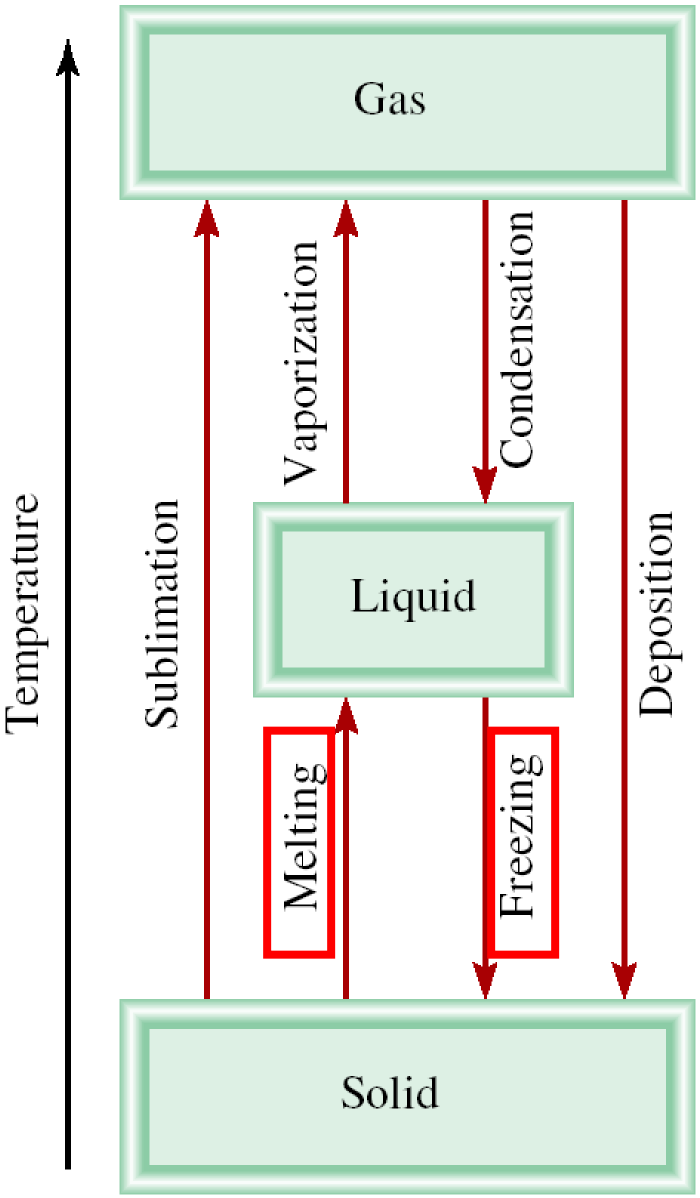


$T < T_c$ $T > T_c$ $T \sim T_c$ $T < T_c$

Solid-Liquid Equilibrium

$$H_2O\ (s) \rightleftharpoons H_2O\ (l)$$

The ***melting point*** of a solid or the ***freezing point*** of a liquid is the temperature at which the solid and liquid phases coexist in equilibrium.

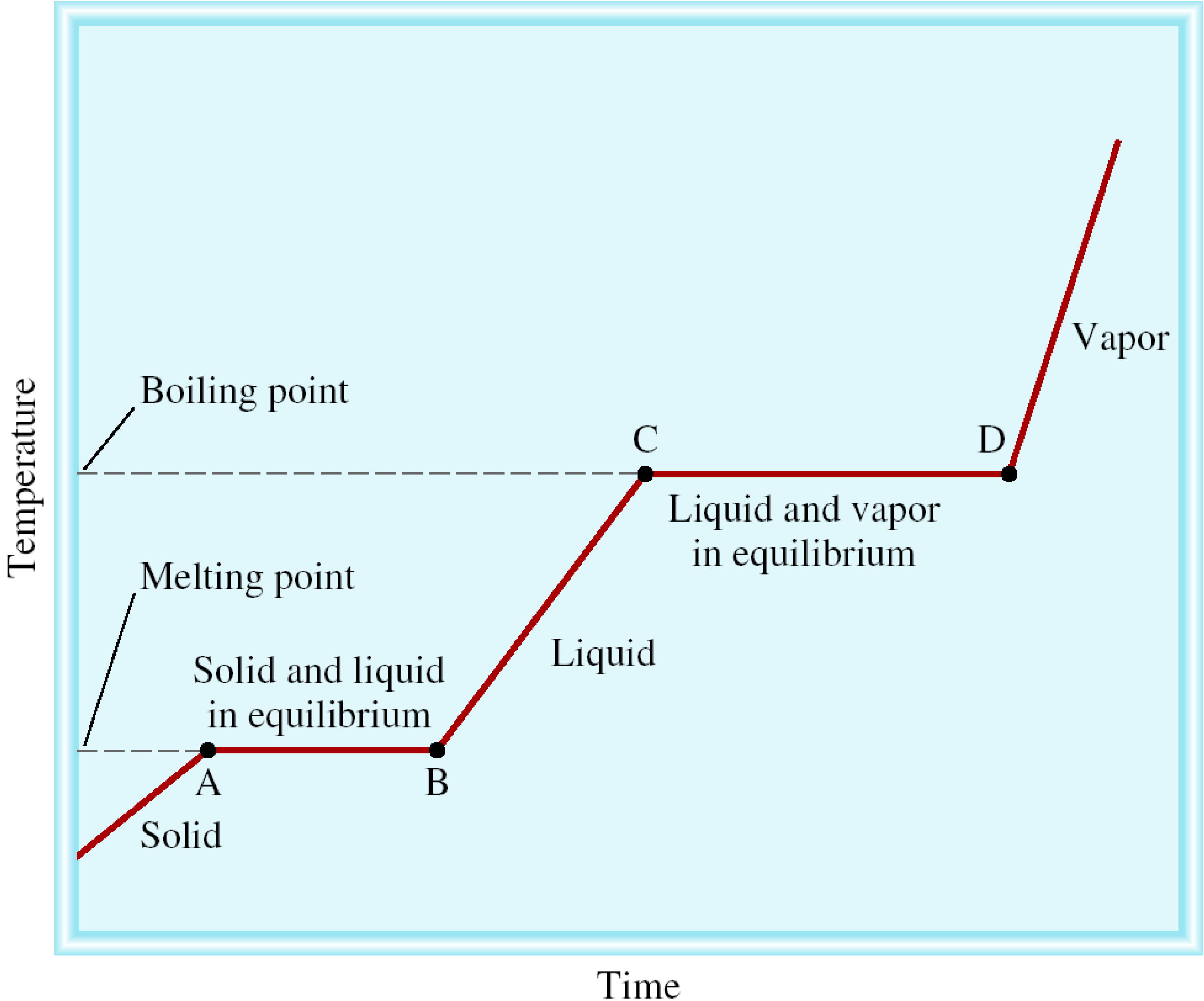


Molar heat of fusion (ΔH_{fus}) is the energy required to melt 1 mole of a solid substance at its freezing point.

Table 12.7 Molar Heats of Fusion for Selected Substances

Substance	Melting Point* (°C)	ΔH_{fus} (kJ/mol)
Argon (Ar)	−190	1.3
Benzene (C_6H_6)	5.5	10.9
Diethyl ether ($C_2H_5OC_2H_5$)	−116.2	6.90
Ethanol (C_2H_5OH)	−117.3	7.61
Mercury (Hg)	−39	23.4
Methane (CH_4)	−183	0.84
Water (H_2O)	0	6.01

Heating Curve



Solid-Gas Equilibrium

$$H_2O\ (s) \rightleftharpoons H_2O\ (g)$$

Molar heat of sublimation (ΔH_{sub}) is the energy required to sublime 1 mole of a solid.

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

(Hess's Law)