



# CHEM2100J Chemistry Autumn 2024

## Chapter 09 Physical Equilibrium

**Dr. Milias Liu**

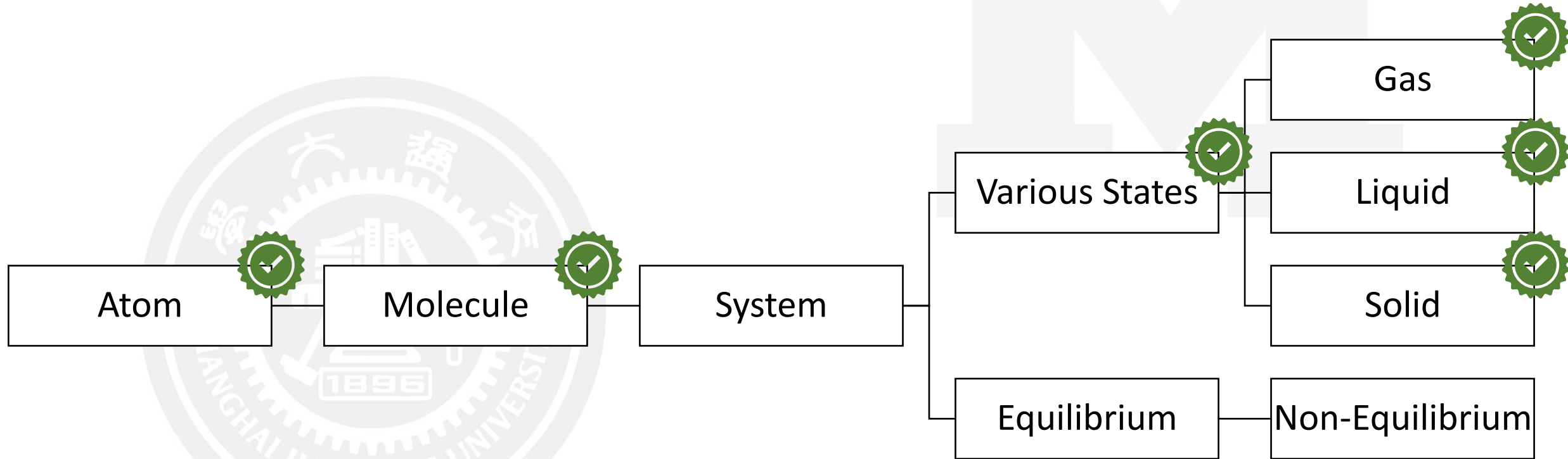
*Assistant Teaching Professor*

UM-SJTU Joint Institute

Room 407A, Longbin Building

[milias.liu@sjtu.edu.cn](mailto:milias.liu@sjtu.edu.cn)

# The Journey So Far



Here:

We explore further the **nature of three states** of matter: solids, liquids, and gases.

We identify how matter **transforms** between each of these states.

We gain a deeper understanding of **solutions**, their composition, and physical properties.

What we learn here helps us understand how to **separate** chemicals from each other.



# One-component System

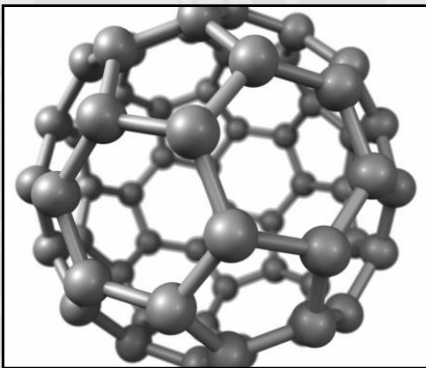
# Phases and Phase Transitions



Diamond



Graphite



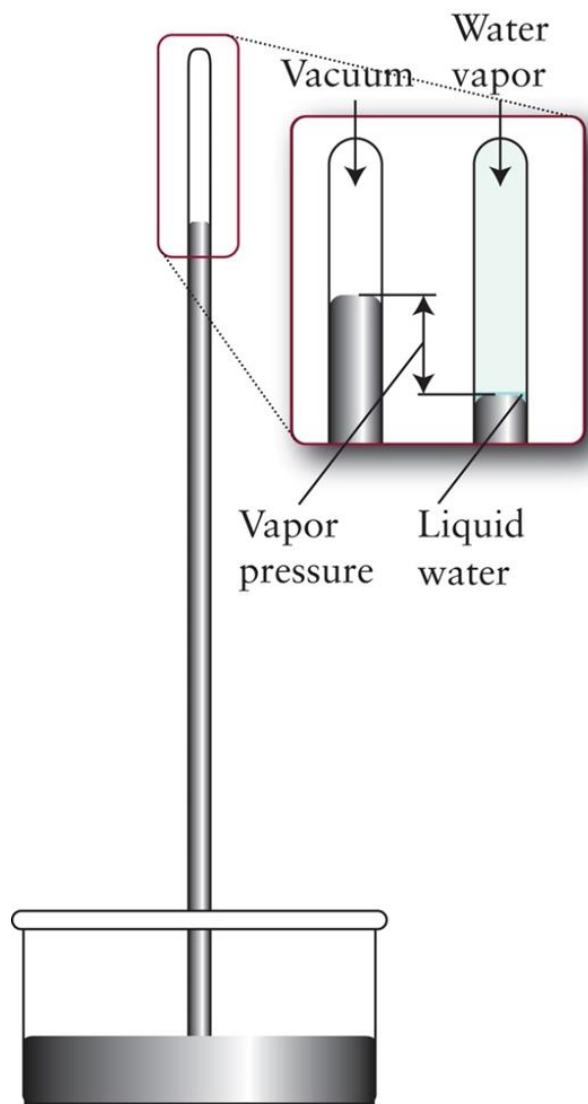
C<sub>60</sub> fullerene

Matter exists in a single phase such as a **solid**, **liquid**, or **gas**. A **phase change** occurs when converting one phase into another.

**Carbon** has three distinct ***solid phases***: diamond, **graphite**, and **Buckminster fullerenes (C<sub>60</sub>)**. **Helium** is only known to exist as a gas and liquid.

Remember (Chapter 8) that phase changes, at constant temperature, are an equilibrium process,  **$\Delta G = 0$** .

# What is Vapour Pressure?



All of the air is evacuated from the tube.

First a tiny drop of water is added at the top:

- All of the water vaporizes.
- The water vapour exerts a force against the mercury, pushing it down.

Second, more water is added:

- However, all added water continues to go into the vapour phase.

Third, still more water is added:

- This time the added water pools up on top of the mercury.
- Once water pools up, we have reached the water vapour pressure.
- The difference in height of mercury levels is the pressure of water vapour.

**Figure 5A.1**  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
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# Vapour Pressure: Volatile



A **volatile** substance has a significant vapour pressure at *ordinary temperatures*.

Methanol (vapour pressure 98 Torr at 20 °C) is highly volatile; mercury (1.4 mTorr) is not.

Solids also exert vapour pressures, but their vapour pressures are low because their molecules are gripped more tightly together.

When a **solid vaporizes** the process is called “**sublimation**”, so a solid has vapour pressure too, although usually negligibly low.

Vapour pressures are often reported in mmHg or Torr.

$$10^5 \text{ Pa} = 1 \text{ bar}$$

$$\begin{aligned} 760 \text{ mmHg} &= 760.000123 \text{ Torr} \\ &\approx 760 \text{ Torr} \\ &= 1 \text{ atm} \\ &= 14.7 \text{ lbf}\cdot\text{in}^{-2} \text{ (PSI)} \\ &= 1.01325 \times 10^5 \text{ Pa} \\ &= 1.01325 \text{ bar} \end{aligned}$$



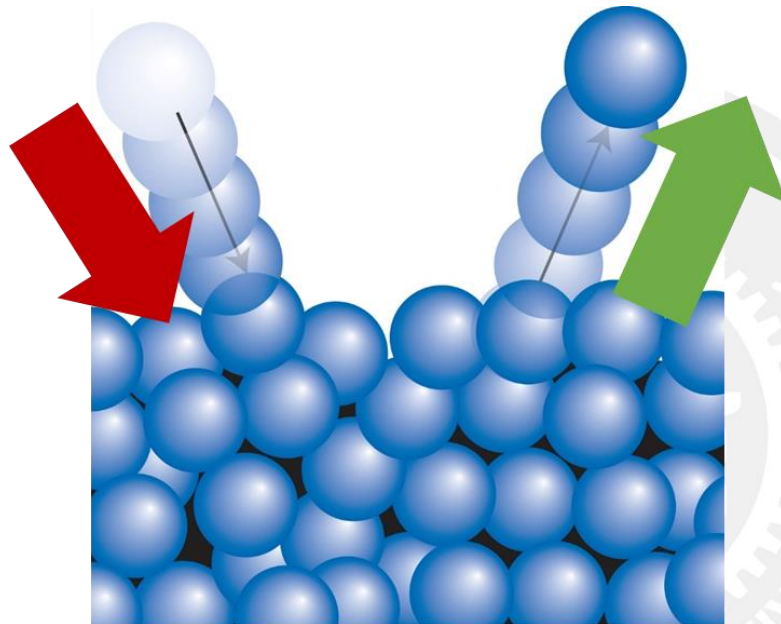
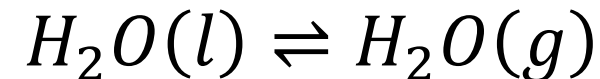


Figure 5A.2  
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Evaporation takes place at the surface because molecules are bound to fewer neighbours.

A **dynamic equilibrium** is when the **rate** of **escaping** matches the **rate** of **returning**. For liquid water and its vapour this is denoted:



*rate of evaporation = rate of condensation*



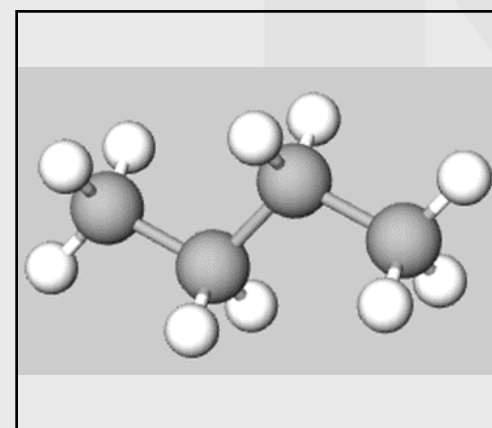
# Volatility and Intermolecular Forces



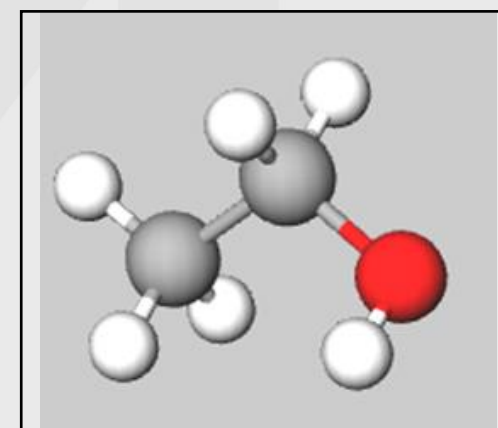
The strength of the intermolecular forces determines a substance's vapour pressure.

Solids and gases aside, liquids with **weak intermolecular forces** have the **highest vapour pressure**.

Liquids with **strong intermolecular forces**, for example ones capable of **forming hydrogen bonds**, have the **lowest vapour pressure**.

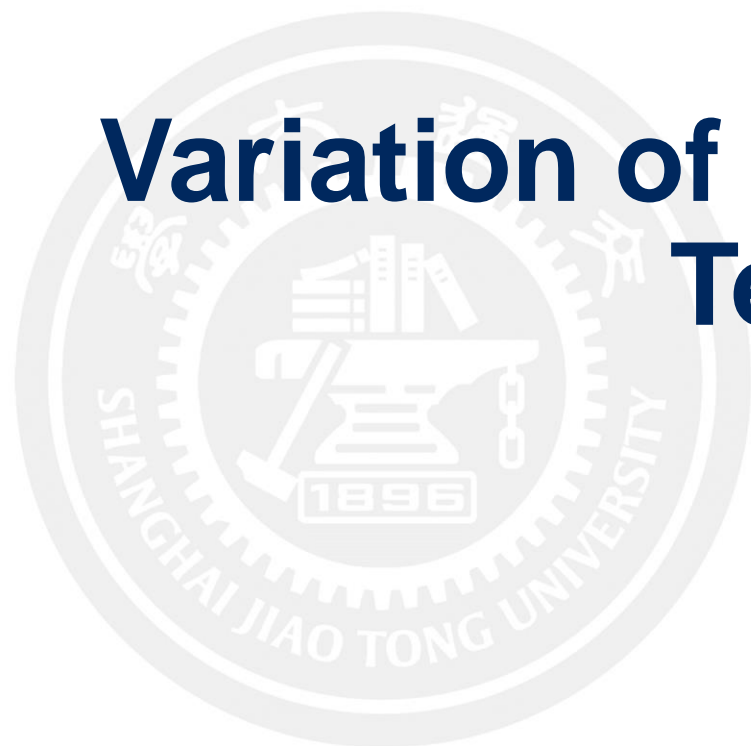


Butane ( $\text{C}_4\text{H}_{10}$ )  
1650 Torr



Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ )  
43.7 Torr

# Variation of Vapour Pressure with Temperature



# Clausius-Clapeyron Equation



$$\ln \left( \frac{p_2}{p_1} \right) = \frac{\Delta H_{vap}^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

Vapour pressure increases with increasing temperature because:

- $\frac{1}{T_1} - \frac{1}{T_2}$  is positive, and  $\Delta H_{vap}^\circ$  is always positive.
- Therefore,  $\ln \left( \frac{p_2}{p_1} \right)$  is also positive, meaning  $p_2 > p_1$ .

$\Delta H_{vap}^\circ$  is a measure of the intermolecular interaction strength (ion–dipole, dipole–dipole, hydrogen bonding, London forces).

*See textbook for derivation.*

# Example



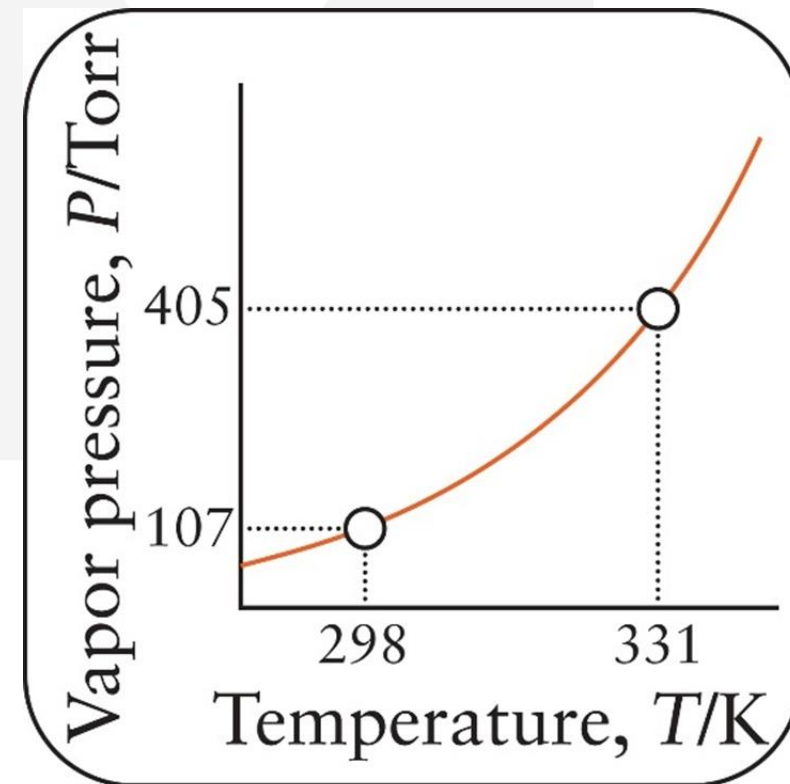
Tetrachloromethane,  $\text{CCl}_4$ , which is now known to be carcinogenic, was once used as a dry-cleaning solvent. The  $\Delta H_{vap, \text{CCl}_4}^\circ = 33.05 \frac{\text{kJ}}{\text{mol}}$  and its vapour pressure at  $57.8^\circ\text{C}$  is 405 Torr. What is the vapour pressure of  $\text{CCl}_4$  at  $25.0^\circ\text{C}$ ?

$$\ln\left(\frac{p_2}{p_1}\right) = \frac{\Delta H_{vap}^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$p_2 = p_1 \cdot e^{\frac{\Delta H_{vap}^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$$p_2 = 405 \text{ Torr} \cdot e^{\frac{3.305 \times 10^4 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}} \left(\frac{1}{(57.8 + 273.15)\text{K}} - \frac{1}{(25.0 + 273.15)\text{K}}\right)} = 107 \text{ Torr}$$

Dry cleaning is NOT a dry process!



Atkins, Chemical Principles: The Quest for Insight, 7e  
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The vapour pressure of water at  $25.0^\circ\text{C}$  is around 20 Torr.

$$T_{b,H_2O} = 100\text{ }^{\circ}\text{C}$$

$$T_{b,Au} = 2807\text{ }^{\circ}\text{C}$$

The **normal boiling point**,  $T_b$ , is the temperature a substance boils at when the pressure is 1 atm (760 Torr, 101,325 Pa).

At lower pressures, the boiling point **decreases**. For instance, at the summit of Mt. Everest the pressure is about 240 Torr and water boils at only 70 °C.

# Example



The vapour pressure of ethanol at 34.9 °C is 13.3 kPa. Use  $\Delta H_{vap}^{\circ} = 43.5 \frac{\text{kJ}}{\text{mol}}$  to estimate the normal boiling point of ethanol.

$$\ln \left( \frac{p_2}{p_1} \right) = \frac{\Delta H_{vap}^{\circ}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$T_1 = \frac{1}{\ln \left( \frac{p_2}{p_1} \right) \cdot \frac{R}{\Delta H_{vap}^{\circ}} + \frac{1}{T_2}}$$

$$T_1 = \frac{1}{\ln \left( \frac{13.3 \text{ kPa}}{101.325 \text{ kPa}} \right) \cdot \frac{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}}{4.35 \times 10^4 \frac{\text{J}}{\text{mol}}} + \frac{1}{(273.15 + 34.9) \text{ K}}} = 350 \text{ K} = 77 \text{ }^{\circ}\text{C}$$

# Freezing and Melting



$$T_{m,H_2O} = 0.0\text{ }^{\circ}\text{C}$$

$$T_{m,Au} = 1064\text{ }^{\circ}\text{C}$$

Solids melt when molecules gain enough energy to wriggle past their neighbours.

The **normal melting point**,  $T_m$ , is the temperature a solid melts at 1 atm.

The *melting temperature* is the same as the *freezing temperature*.



# Density Anomaly of Water

Most substances are denser in the solid phase than liquid, *water being an exception.*

Water is highly unusual, at 0.0 °C:

$$\rho_{\text{liquid}} > \rho_{\text{solid}}$$

Ice floats on water.

Solid water hydrogen bonds hold the molecules apart at low temperatures.

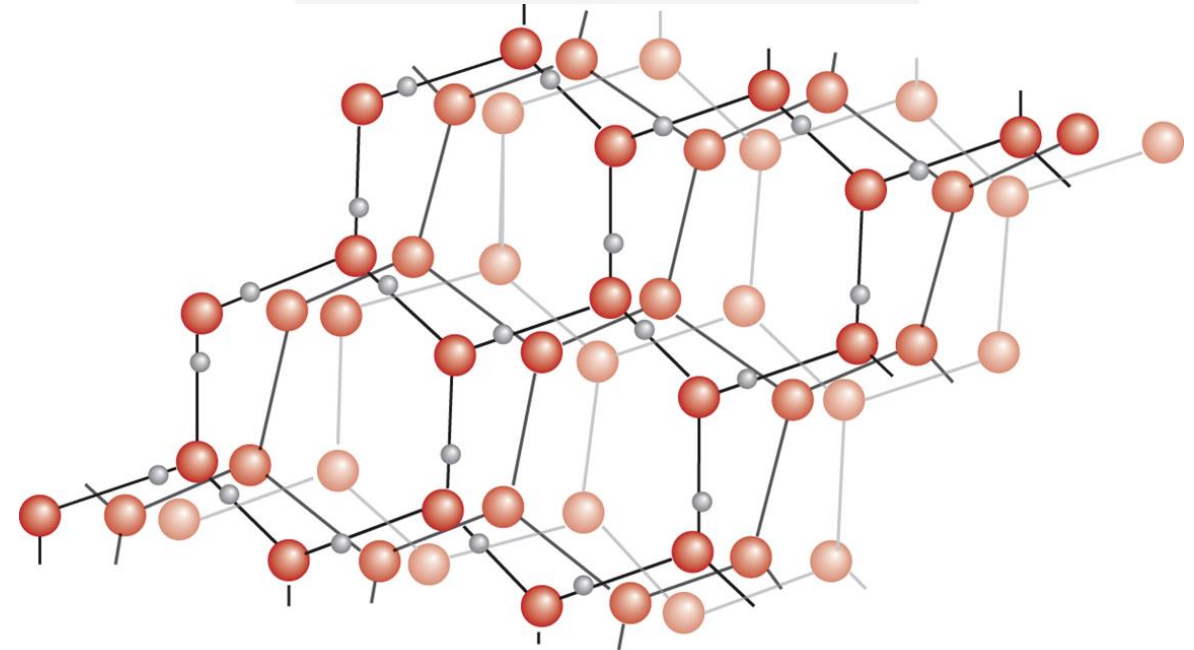


Figure 5B.1

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# Density Anomaly of Water



As ice melts, the hydrogen bonds collapse, allowing water molecules to pack more closely.

## Why is ice slippery?

Pressure melting?

$$T_{m,1 \text{ atm}} = 0 \text{ }^{\circ}\text{C} \quad T_{m,400 \text{ atm}} = -3 \text{ }^{\circ}\text{C}$$

However, best skating temperature  $-5 \text{ }^{\circ}\text{C}$ , and at  $-40 \text{ }^{\circ}\text{C}$  (north or south poles) skating is still possible

## Semi-liquid state lubrication layer

Water molecules on the surface are not as tightly bound as those in the bulk below. They are less mobile than in liquid water but much more mobile than the bulk molecules

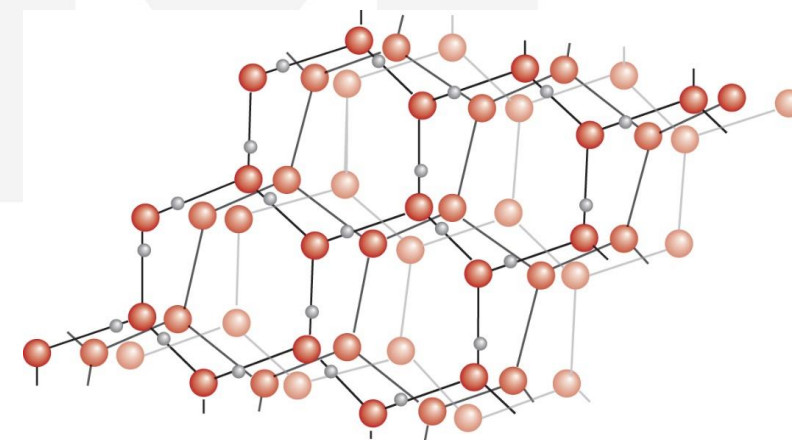


Figure 5B.1  
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# Phase Diagram



A phase diagram is a map showing phases at different pressures and temperatures.

The region marked "**solid**" is the solid phase of a substance. Other regions are marked "**liquid**" and "**vapour**".

This phase diagram shows that carbon dioxide at 10 °C and 2 atm will be a gas. At 10 atm and 10 °C, CO<sub>2</sub> will condense into a liquid.

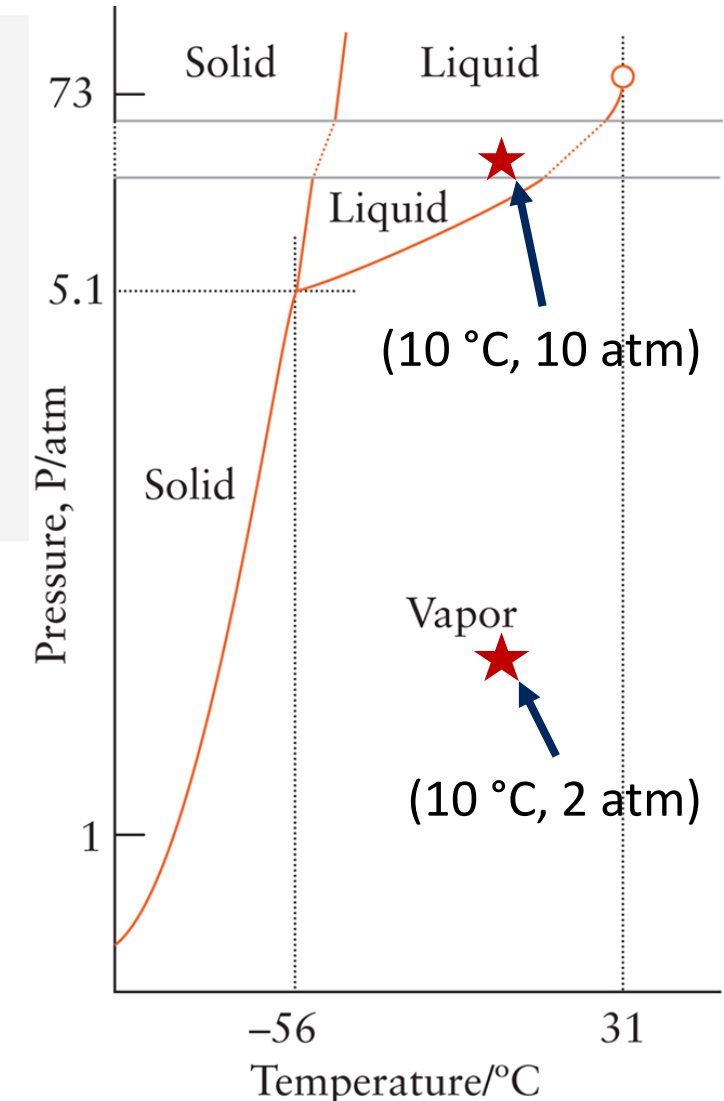


Figure 5B.3

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A triple point is the temperature and pressure at which water exists as a **solid**, **liquid**, and **vapour**.

The **slope** of the solid–liquid boundary depends on the relative **density**. And liquid water is denser than solid ice.

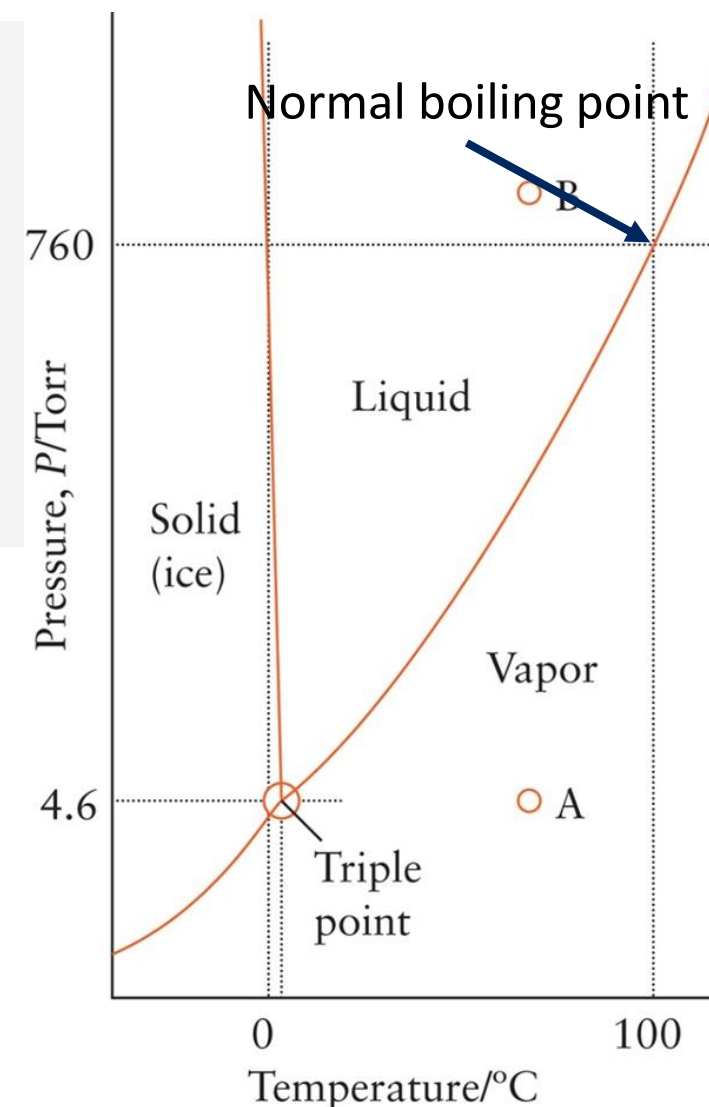


Figure 5B.2

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# Short Quiz



From the phase diagrams to the right, predict which is denser, the solid or the liquid phase. Explain your conclusion.

CO<sub>2</sub>

The solid, because it is the stable phase at higher pressures.

H<sub>2</sub>O

The **slope** of the solid–liquid boundary reveals that the density of liquid water is higher than that of ice.

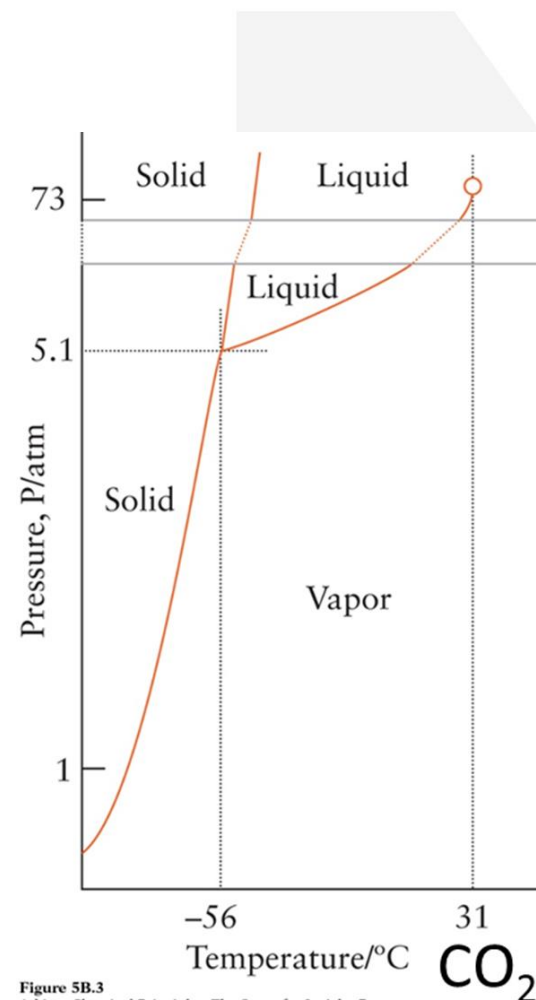


Figure 5B.3  
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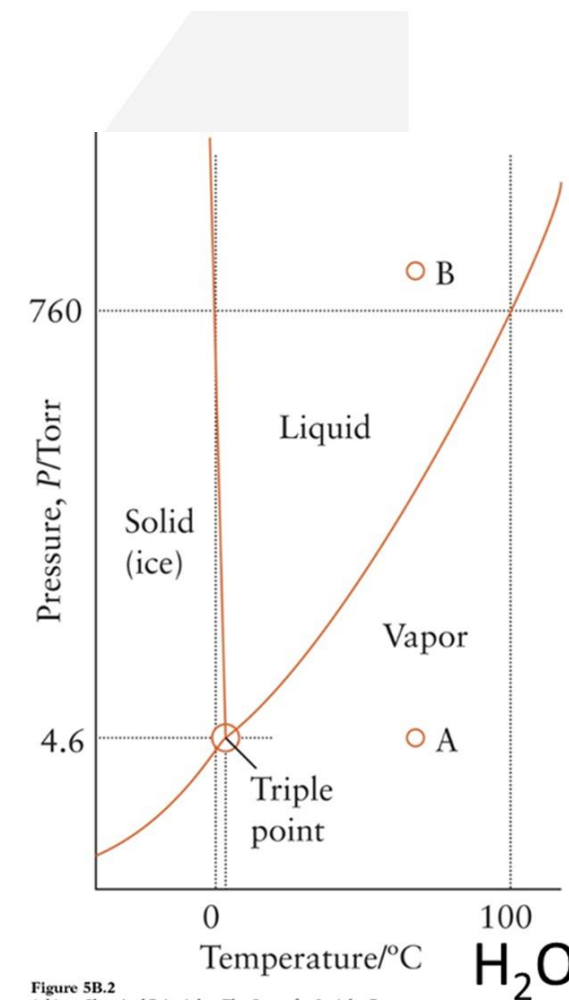


Figure 5B.2  
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# Sulfur, S<sub>8</sub>

Sulfur has two solid phases, rhombic and monoclinic, for the two ways its crownlike S<sub>8</sub> molecules stack.

Sulfur has three triple points, and four different phases.

Many substances have several solid phases. A "quadruple point" has never been observed.

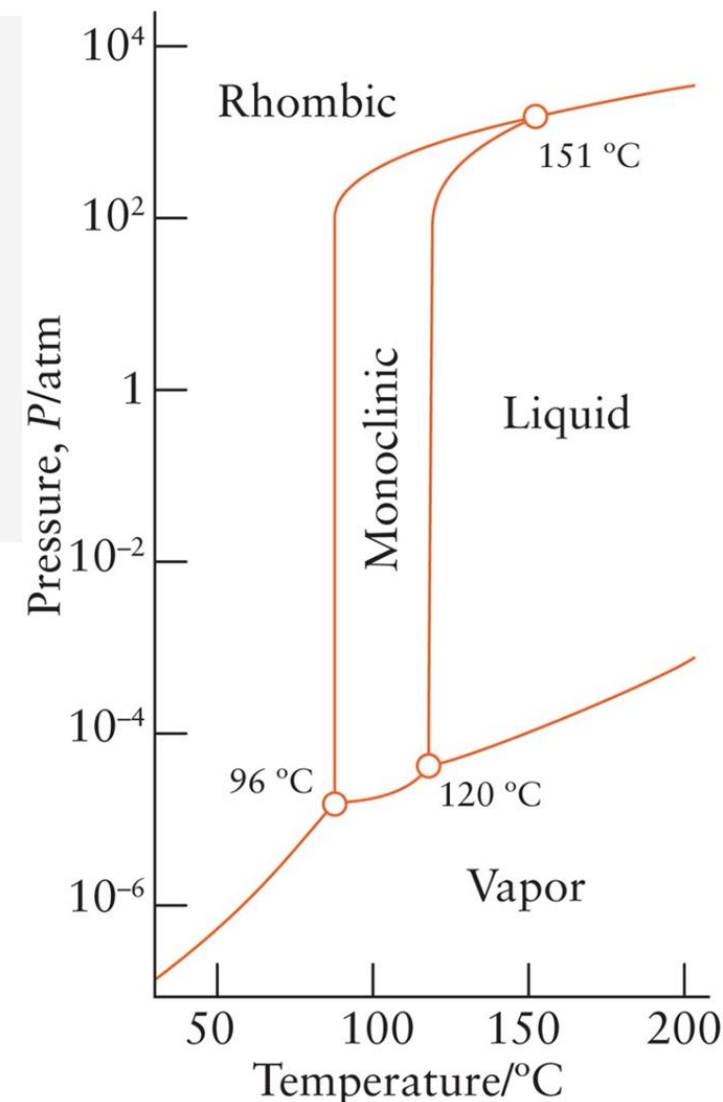
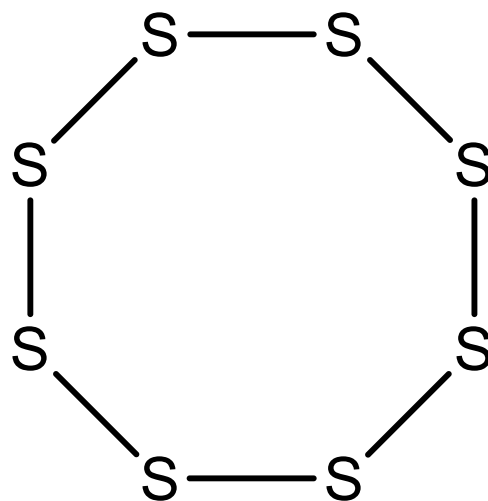


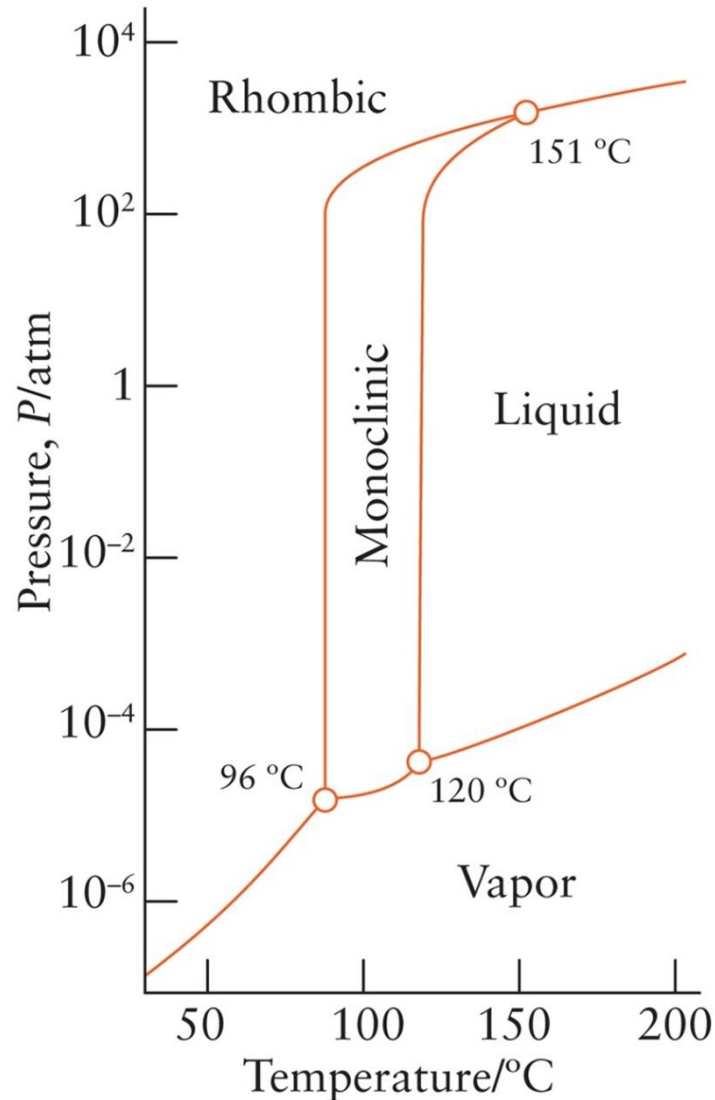
Figure 5B.4

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# Short Quiz



From the phase diagram for sulfur, predict which phase is more dense, liquid sulfur or monoclinic sulfur. Explain your conclusion.

The positive slope indicates the monoclinic is denser. Higher pressures indicate formation of a solid.

Figure 5B.4  
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# Water's Multiple Solid Phases



Water, like sulfur, has different phases.

The phase diagram of water is drawn logarithmically, in order to show the different solid phases of water.

Ice-VII is stable only above 20,000 atm and 100 °C.

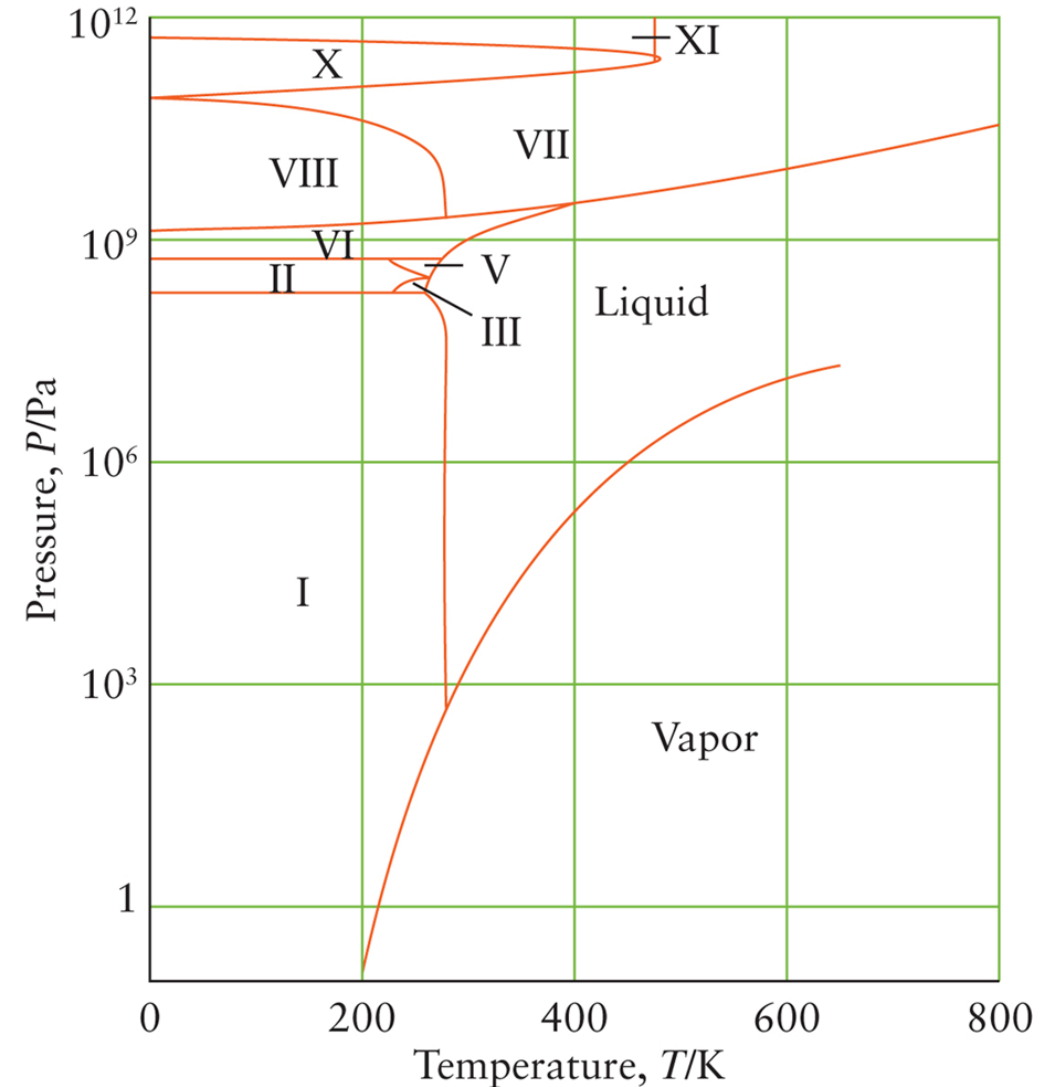
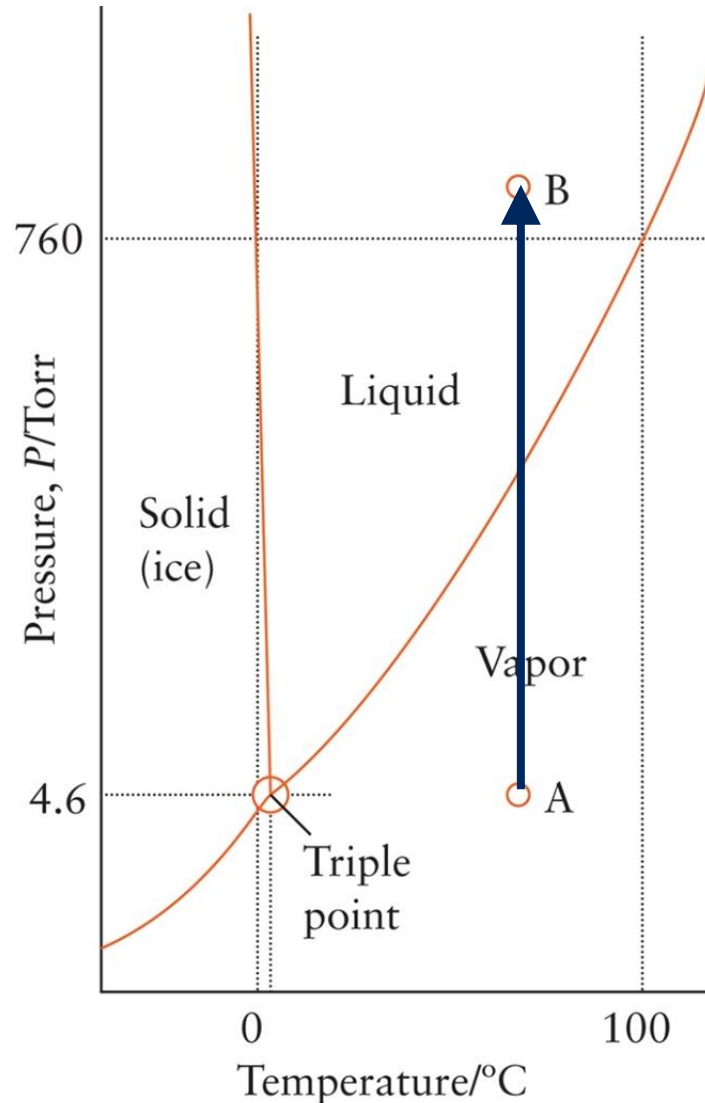


Figure 5B.5

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# Example



Use the phase diagram to describe the physical states and phase changes of water as the pressure on it is increased from 5 Torr (point A) to 800 Torr (point B) at 70 °C.

Point A is at 5 Torr and 70 °C, where water is a vapour. Increasing the pressure passes the liquid-vapour phase boundary, at which point liquid begins to form. At 800 Torr, point B, the water is in the liquid region.

Figure 5B.2  
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# Critical Properties

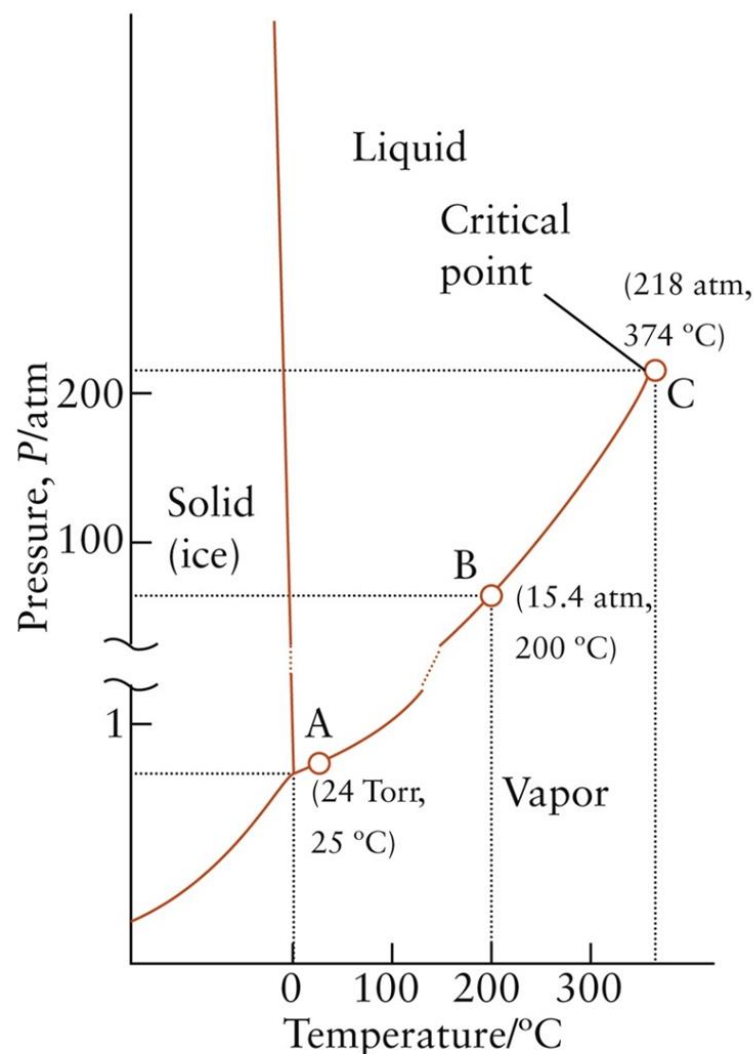


Figure 5B.8  
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There is an end in the liquid–vapour phase boundary called the critical point.

The **density of the vapour** is so great that it is **equal** to the **density of the liquid**.

The **surface boundary disappears** into a single, **uniform phase**.

Here, the critical pressure and critical temperature mark the end of either liquid or vapour, and is now a **supercritical fluid**, a very dense vapour.

# Critical Point: Vapour Density = Liquid Density



Figure 5B.9

Atkins, *Chemical Principles: The Quest for Insight*, 7e

Courtesy Professor Walter Leitner, RWTH Aachen University, and Dr. Nils Theyssen, Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr, Germany.

Increasing the temperature of a liquid in a sealed container to a point where...

*the liquid density decreases, and the vapour density increases...*

and a single phase exists beyond the **critical** pressure and temperature.



# Supercritical Fluid Region



Supercritical fluid is gas and also liquid. It can effuse through solids like a gas and dissolve matter like a liquid.

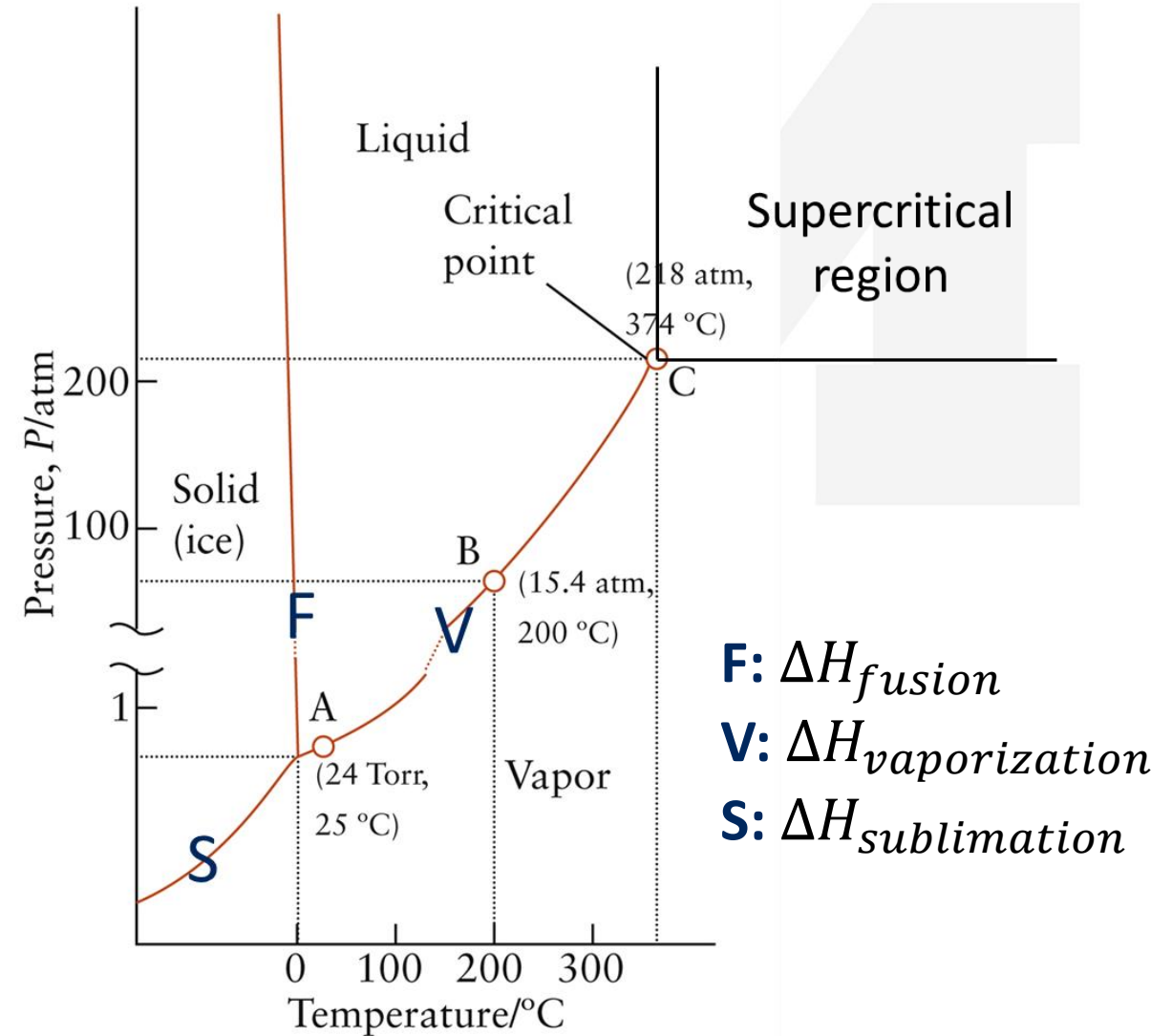


Figure 5B.8

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# Example

Identify trends in the effect of hydrogen bonding on the critical temperature.

For polar molecules like  $\text{H}_2\text{O}$  and  $\text{NH}_3$ , a higher critical temperature and pressure indicate it takes **more energy** to force these types of molecules into a supercritical phase.

For nonpolar molecules, London forces dominate, and show that it takes **less energy** to put the molecules into a supercritical phase.

Substance	$T_c / ^\circ\text{C}$	$p_c / \text{atm}$
He	-268	2.3
Ne	-229	27
Ar	-123	48
Kr	-64	54
Xe	17	58
$\text{H}_2$	-240	13
$\text{O}_2$	-118	50
$\text{H}_2\text{O}$	374	218
$\text{N}_2$	-147	34
$\text{NH}_3$	132	111
$\text{CO}_2$	31	73
$\text{CH}_4$	-83	46
$\text{C}_6\text{H}_6$	289	49



# Multiple-component System (Binary)



# Lowering of Vapour Pressure



The French scientist Francois-Marie Raoult, discovered that, at any temperature, the vapour pressure of a solvent is proportional to its mole fraction in a solution. Now known as **Raoult's law**:

$$p_{\text{solvent}} = \chi_{\text{solvent}} \cdot p_{\text{pure solvent}}$$

$p_{\text{solvent}}$  is the vapour pressure of the solvent,  $\chi_{\text{solvent}}$  is the mole fraction of the **solvent**, and  $p_{\text{pure solvent}}$  is the vapour pressure of the pure solvent.

# Example



Calculate the vapour pressure of water at 20 °C in a solution prepared by dissolving 10.00 g of the nonelectrolyte sucrose,  $C_{12}H_{22}O_{11}$ , in 100.0 g of water.

$$p_{H_2O,pure} = 17.54 \text{ Torr}$$

$$p_{\text{solvent}} = \chi_{\text{solvent}} \cdot p_{\text{pure solvent}}$$

$$p_{\text{solvent}} = \frac{n_{\text{solvent}}}{n_{\text{solute}} + n_{\text{solvent}}} \cdot p_{\text{pure solvent}}$$

$$p_{H_2O} = \frac{n_{H_2O}}{n_{C_{12}H_{22}O_{11}} + n_{H_2O}} \cdot p_{H_2O,pure}$$

# Example



$$p_{H_2O} = \frac{n_{H_2O}}{n_{C_{12}H_{22}O_{11}} + n_{H_2O}} \cdot p_{H_2O,pure}$$

$$p_{H_2O} = \frac{\frac{m_{H_2O}}{M_{H_2O}}}{\frac{m_{C_{12}H_{22}O_{11}}}{M_{C_{12}H_{22}O_{11}}} + \frac{m_{H_2O}}{M_{H_2O}}} \cdot p_{H_2O,pure} = \frac{\frac{100.0 \text{ g}}{18.015 \frac{\text{g}}{\text{mol}}}}{\frac{10.00 \text{ g}}{342.2 \frac{\text{g}}{\text{mol}}} + \frac{100.0 \text{ g}}{18.015 \frac{\text{g}}{\text{mol}}}} \times 17.54 \text{ Torr}$$

$$p_{H_2O} = 0.995 \times 17.54 \text{ Torr} = 17.45 \text{ Torr}$$

# Binary Liquid Mixtures

Liquids A, benzene,  $\text{C}_6\text{H}_6$ , and B toluene ( $\text{C}_6\text{H}_5\text{CH}_3$ ), are nearly ideal when mixed, as these two compounds have similar molecular structures.

We can treat ideal mixtures using Raoult's law:

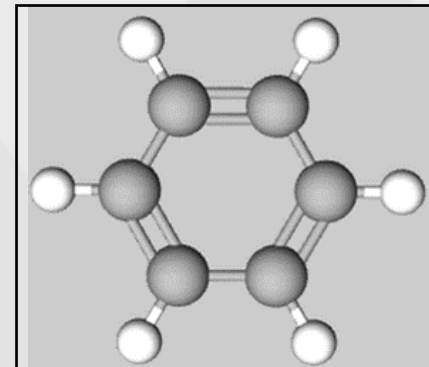
$$p_{\text{solvent}} = \chi_{\text{solvent}} \cdot p_{\text{pure solvent}}$$

$$p_A = \chi_{A,\text{liquid}} \cdot p_{A,\text{pure}} \text{ and } p_B = \chi_{B,\text{liquid}} \cdot p_{B,\text{pure}}$$

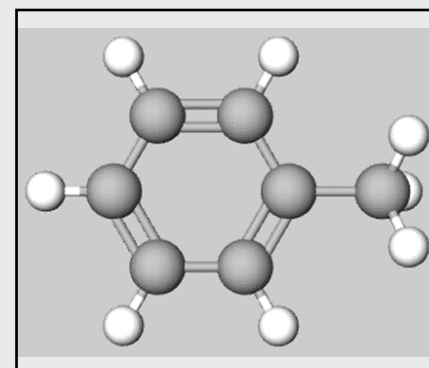
According to Dalton's law, the total pressure of the vapour,  $p_{\text{total}}$ , is the sum or **total** of these two partial pressures:

$$p_{\text{total}} = p_A + p_B$$

$$p_{\text{total}} = \chi_{A,\text{liquid}} \cdot p_{A,\text{pure}} + \chi_{B,\text{liquid}} \cdot p_{B,\text{pure}}$$

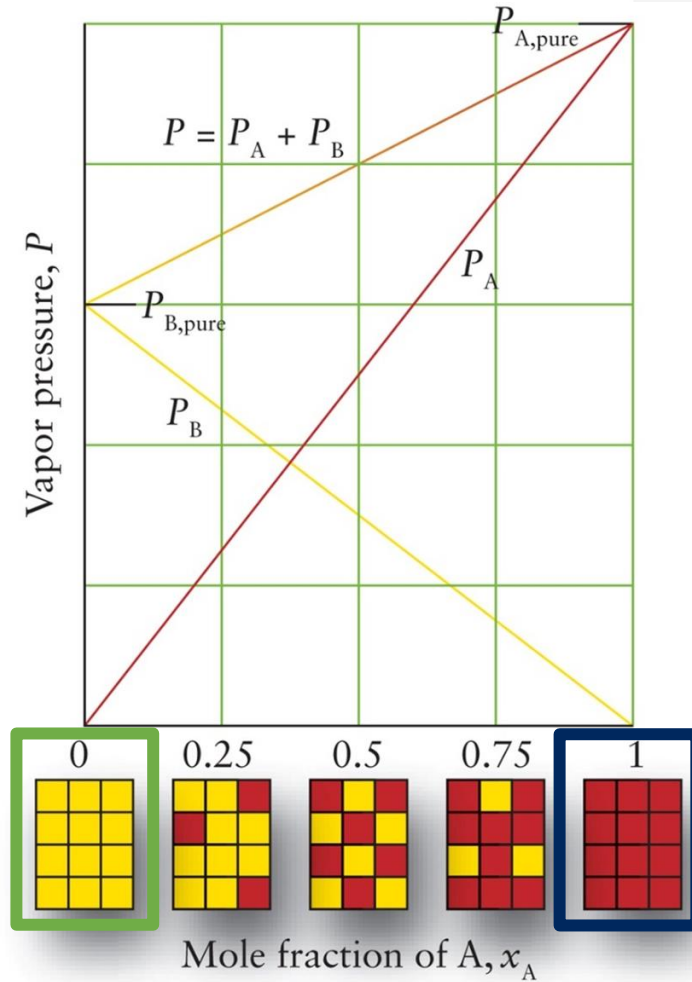


Benzene  
 $\text{C}_6\text{H}_6$



Toluene  
 $\text{C}_6\text{H}_5\text{CH}_3$

# Binary Liquid Mixtures



Pure solute

Pure solvent

**Figure 5C.2**  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
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# Example



What is the vapour pressure of each component at 25 °C and the total vapour pressure of a mixture in which one-third of the molecules are benzene ( $\chi_{benzene,liquid} = \frac{1}{3}$ ,  $\chi_{toluene,liquid} = \frac{2}{3}$ )? The vapour pressures of pure benzene and pure toluene at 25 °C are 94.6 and 29.1 Torr, respectively.

$$p_{benzene} = \chi_{benzene,liquid} \cdot p_{benzene,pure} = \frac{1}{3} \times 94.6 \text{ Torr} = 31.5 \text{ Torr}$$

$$p_{toluene} = \chi_{toluene,liquid} \cdot p_{toluene,pure} = \frac{2}{3} \times 29.1 \text{ Torr} = 19.4 \text{ Torr}$$

Applying Dalton's law:

$$p_{total} = p_{benzene} + p_{toluene} = 31.5 \text{ Torr} + 19.4 \text{ Torr} = 50.9 \text{ Torr}$$



A hypothetical solution that obeys Raoult's law exactly at all concentrations is called an ***ideal solution***, and if it does not, then it is a ***nonideal solution*** (a limiting law, just like  $pV = nRT$  does not work outside of Standard Temperature and Pressure or during phase changes).

Real solutions are approximately ***ideal*** at concentrations below about **0.1 M for nonelectrolyte** solutions (e.g., sugar) and **0.01 M for electrolyte** solutions (e.g., ionic).

# Finding Quantitative Mole Ratios of Vapour



We were just asked to find the total pressure. What is the composition of that vapour?  
We can use Dalton's law:

$$p_A = \chi_{A,\text{vapour}} \cdot p_{\text{total}}$$

Using  $p_{\text{total}} = p_A + p_B$  (Dalton's law):

$$\chi_{A,\text{vapour}} = \frac{p_A}{p_{\text{total}}} = \frac{p_A}{p_A + p_B} \quad (\text{Note: This is for the vapour, not the liquid!})$$

Substituting  $p_A = \chi_{A,\text{liquid}} \cdot p_{A,\text{pure}}$  (Raoult's law) for each component:

$$\chi_{A,\text{vapour}} = \frac{\chi_{A,\text{liquid}} \cdot p_{A,\text{pure}}}{(\chi_{A,\text{liquid}} \cdot p_{A,\text{pure}}) + (\chi_{B,\text{liquid}} \cdot p_{B,\text{pure}})}$$

We now have an expression that relates **composition of vapour** (**above the liquid**) in terms of **mole fractions of liquids**.

# Example



Find the mole fraction of benzene at 25 °C in the **vapour** of a solution of benzene in toluene in which one-third of the molecules in the liquid are benzene ( $\chi_{benzene,liquid} = \frac{1}{3}$ ,  $\chi_{toluene,liquid} = \frac{2}{3}$ ). The vapour pressures of benzene and toluene at 25 °C are 94.6 and 29.1 Torr, respectively.

$$\chi_{A,vapour} = \frac{\chi_{A,liquid} \cdot p_{A,pure}}{(\chi_{A,liquid} \cdot p_{A,pure}) + (\chi_{B,liquid} \cdot p_{B,pure})}$$

$$\chi_{benzene,vapour} = \frac{\chi_{benzene,liquid} \cdot p_{benzene,pure}}{(\chi_{benzene,liquid} \cdot p_{benzene,pure}) + (\chi_{toluene,liquid} \cdot p_{toluene,pure})} = \frac{\frac{1}{3} \times 94.6 \text{ Torr}}{\left(\frac{1}{3} \times 94.6 \text{ Torr}\right) + \left(\frac{2}{3} \times 29.1 \text{ Torr}\right)} = 0.619$$

$$\chi_A + \chi_B = 1$$

$$\chi_{toluene,vapour} = 1 - \chi_{benzene,vapour} = 1 - 0.619 = 0.381$$

The mole fraction of Benzene in vapour is nearly twice that in the liquid.

# Distillation

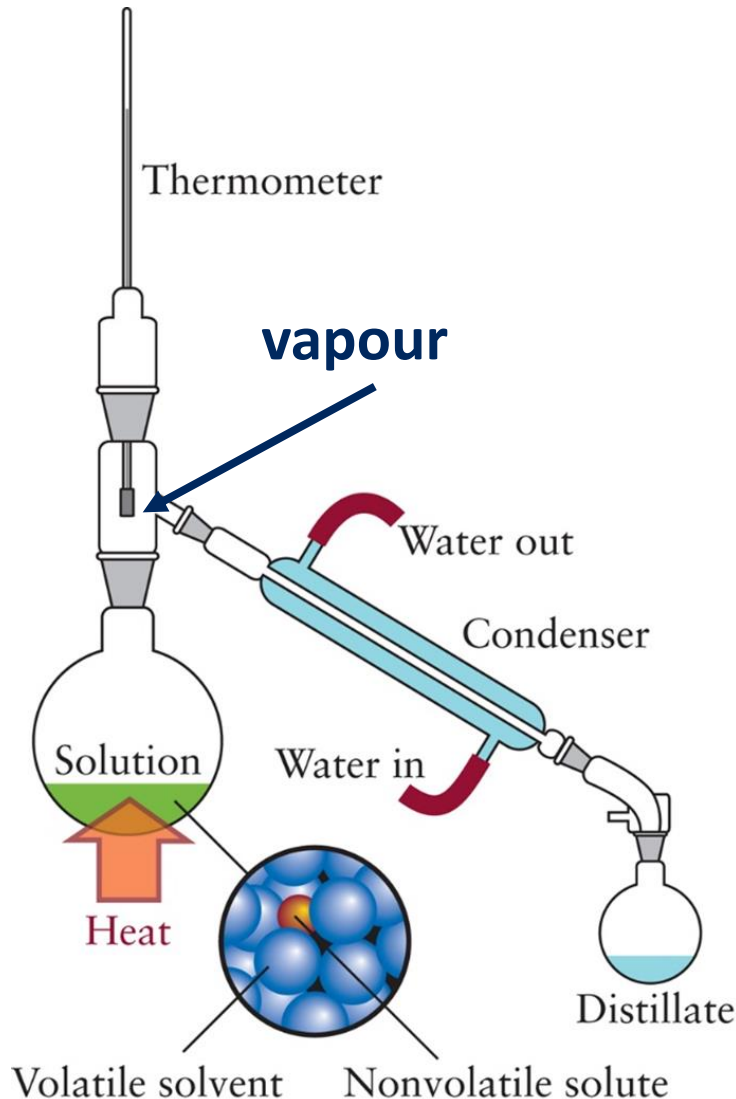


Figure G.6  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
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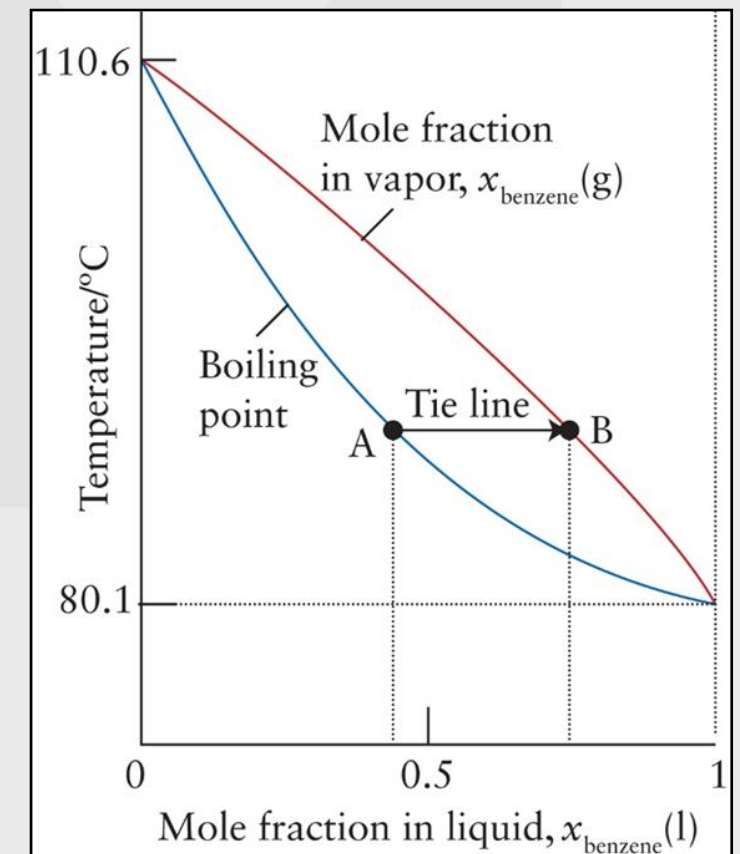
The normal boiling point is at 1 atm.

$$T_{b,\text{benzene}} = 80.1\text{ }^{\circ}\text{C}$$

$$T_{b,\text{toluene}} = 110.6\text{ }^{\circ}\text{C}$$

The **vapour pressure**, as well as the **boiling point** of the mixture will be intermediate between the two pure liquids.

This is called a temperature–composition diagram; the lower curve shows how the normal boiling point of the mixture varies with the composition. To find the composition of the vapour, we simply look along the **tie line**.



A temperature–composition diagram for benzene and toluene.

# Distillation: Benzene and Toluene

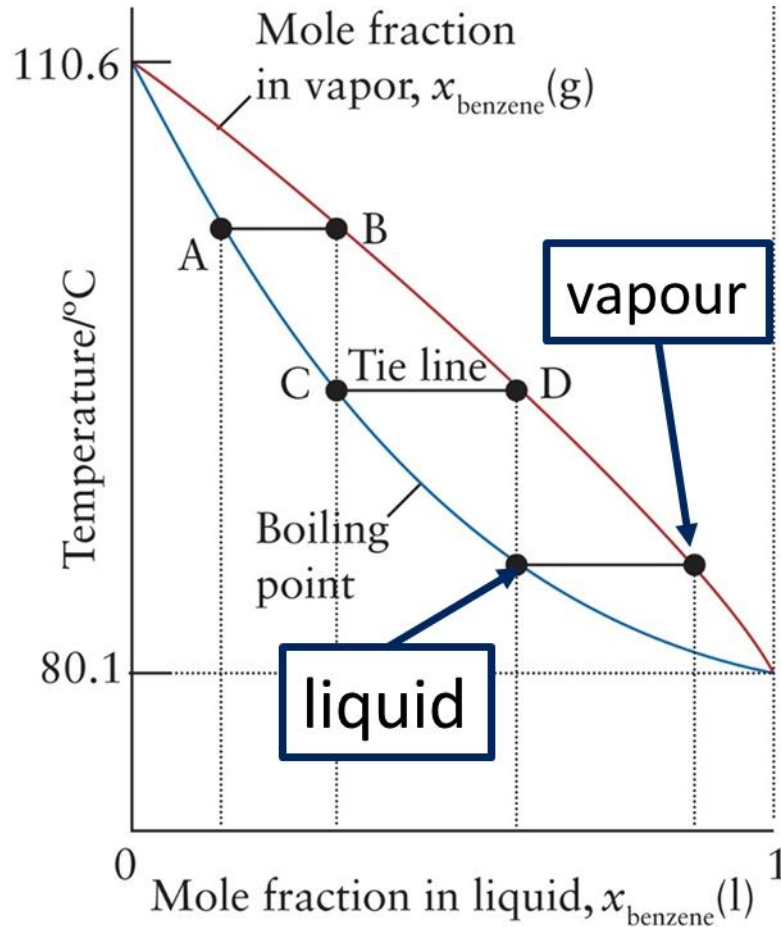


Figure 5C.6  
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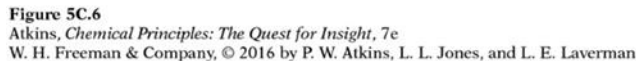
At point A  $\chi_{\text{benzene,liquid}} = 0.20$ . The corresponding vapour (point B) has a composition  $\chi_{\text{benzene,vapour}} = 0.45$ .

Condensing that vapour into a liquid yields a distillate with  $\chi_{\text{benzene,liquid}} = 0.45$ .

Taking this distillate and **reheating** it (point C) leads to a corresponding vapour above the liquid with  $\chi_{\text{benzene,vapour}} = 0.73$  (point D). The concentration increases with each distillation step.



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$$\chi_{benzene,liquid} = 0.73 > \chi_{benzene,liquid} = 0.45$$

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# Industrial Fractional Distillation



Fractional distillation is a continuous re-distillation, using tall columns packed with high surface area glass beads.

Lower  $T_b$  vapour condenses and vaporizes over and over as it rises; the higher  $T_b$  liquid drips back into the boiling mixture.

Vapour becomes richer in the component with the lower boiling point.

The final distillate is nearly pure (lower  $T_b$  liquid), and the liquid in the pot is also nearly pure (higher  $T_b$  liquid).



Figure 5C.8  
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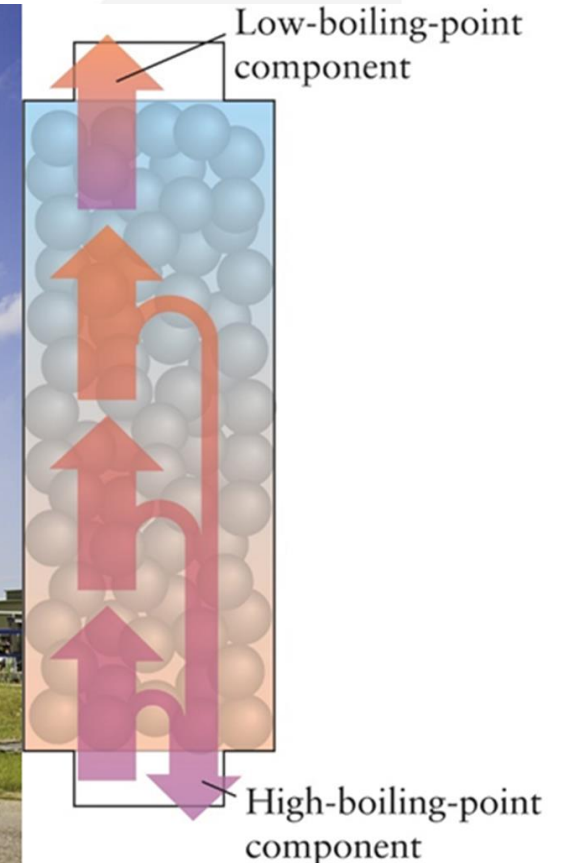


Figure 5C.7  
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# Azeotropes

Most liquids do not follow Raoult's law.

Ethanol and benzene have a positive, **endothermic** enthalpy of mixing; their **vapour pressure** is **higher** than **predicted** and produces a **positive deviation**.

(Solvent and solute repulse each other)

Acetone and chloroform have a negative, **exothermic** enthalpy of mixing; their **vapour pressure** is **lower** than **predicted** and produces a **negative deviation**.

(Solvent and solute attract each other, H-bridge bonds between  $\text{CH}_3\text{COCH}_3$  and  $\text{CHCl}_3$ )

Deviations from Raoult's law **can make it impossible** to separate liquids by distillation.

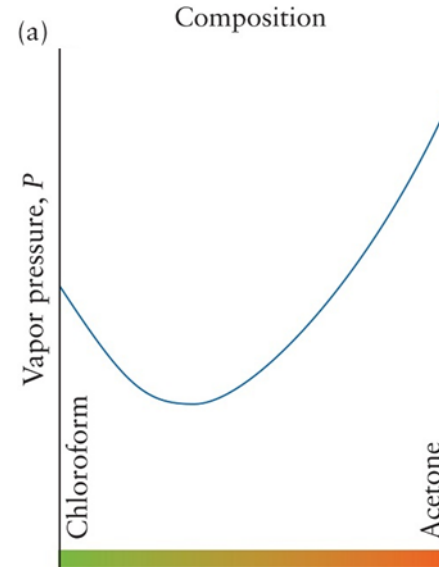
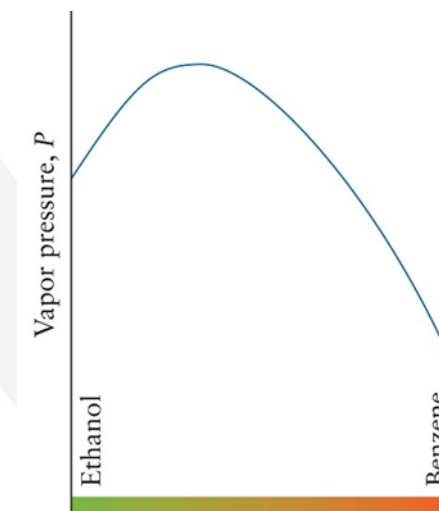
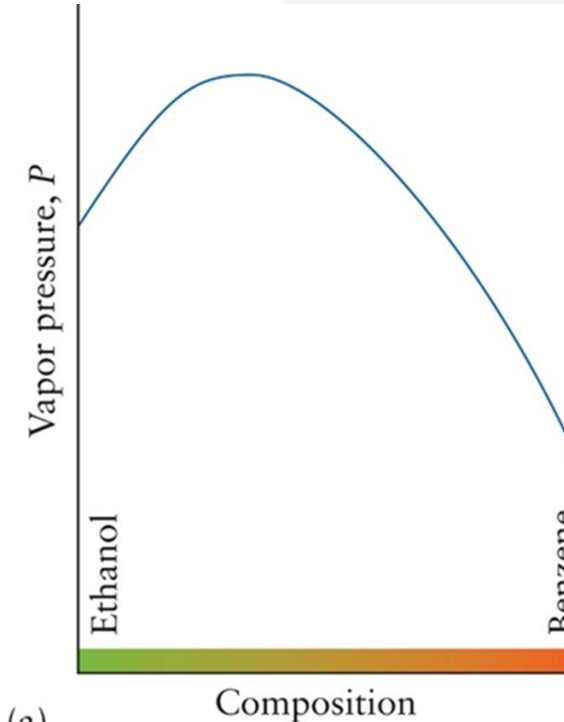


Figure 5C.9b  
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# Azeotropes

A positive deviation from Raoult's law means that the *attractive forces* between solute and solvent are **lower** than the pure component. (Solvent and solute repulse each other)

As a result, the boiling point of the mixture is **lower than that predicted** by Raoult's law and it boils more easily.



(a)  
Figure 5C.9a  
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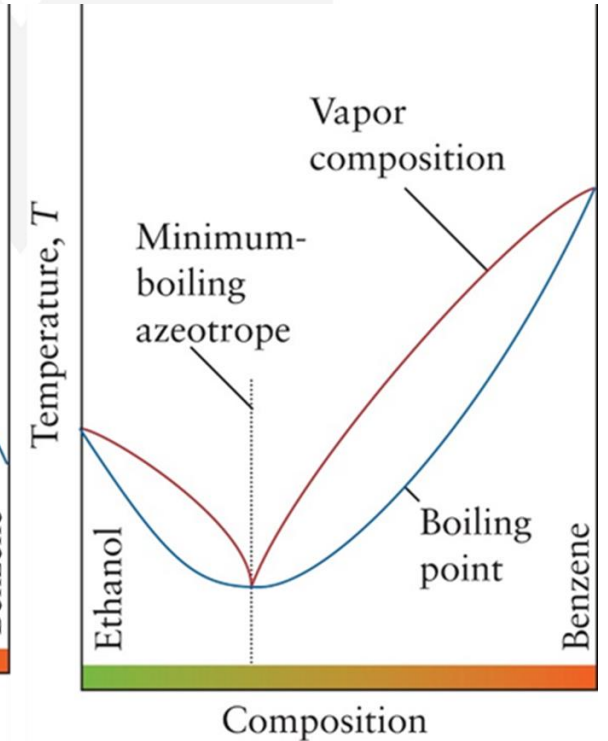


Figure 5C.10  
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# Gases Dissolve Into Liquids

Oxygen, vital to all aquatic organisms, is **nonpolar** yet is slightly soluble in water (polar).

Pressure of a gas is a determining solubility factor.

First observed in 1801 by the English chemist William Henry, it is now known as **Henry's law**.

# Pressure and Gas Solubility: Henry's Law



The **solubility** of a **gas** is **directly proportional** to its **partial pressure**:

$k_H$  is called Henry's constant

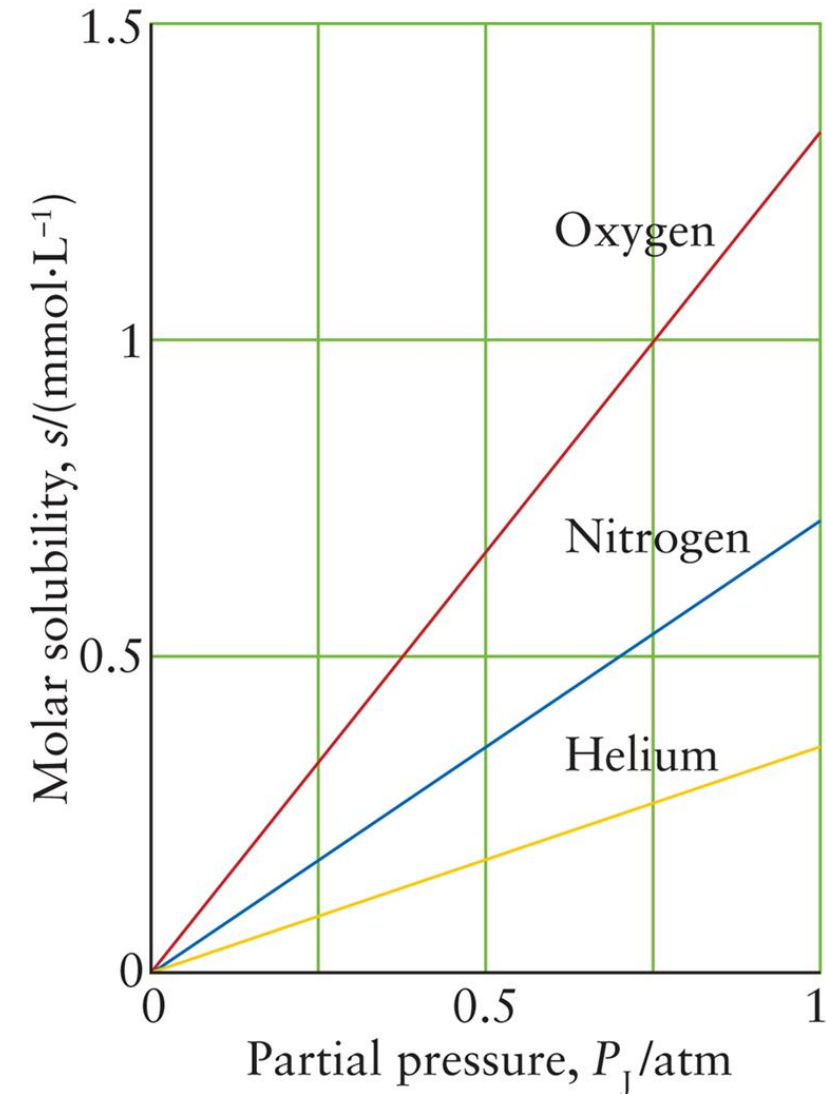


Figure 5D.8

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# Example

Verify that the concentration of oxygen in lake water is adequate to sustain aquatic life, which requires a concentration of at least  $0.13 \text{ mmol} \cdot \text{L}^{-1}$ . The partial pressure of oxygen is  $0.21 \text{ atm}$  at sea level.

$$k_{H,O_2} = 1.3 \times 10^{-3} \frac{\text{mol}}{\text{L} \cdot \text{atm}}$$

$$s = k_H \cdot p_{\text{gas}}$$

$$s = 1.3 \times 10^{-3} \frac{\text{mol}}{\text{L} \cdot \text{atm}} \times 0.21 \text{ atm} = 0.27 \frac{\text{mmol}}{\text{L}}$$

$$0.27 \frac{\text{mmol}}{\text{L}} > 0.13 \frac{\text{mmol}}{\text{L}}$$





# Solids Dissolve Into Liquids

# Enthalpy of Solution



Measuring heat **released** or **absorbed** when a substance dissolves is called molar enthalpy of solution,  $\Delta H_{sol}$ .

Lithium chloride dissolves **exothermically** (heat releasing). Others, such as ammonium nitrate, dissolve **endothermically** (heat absorbing).

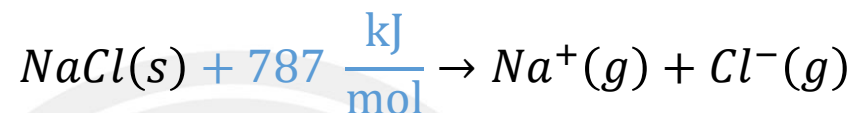
	$\Delta H_{sol}^{\circ} / \text{kJ}\cdot\text{mol}^{-1}$							
	Anion							
Cation	F <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>	OH <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>
Li <sup>+</sup>	+4.9	-37.0	-48.8	-63.3	-23.6	-18.2	-2.7	-29.8
Na <sup>+</sup>	+1.9	+3.9	-0.6	-7.5	-44.5	-26.7	+20.4	-2.4
K <sup>+</sup>	-17.7	+17.2	+19.9	+20.3	-57.1	-30.9	+34.9	-23.8
NH <sub>4</sub> <sup>+</sup>	-1.2	+14.8	+16.0	+13.7	-	-	+25.7	+6.6
Ag <sup>+</sup>	-22.5	+65.5	+84.4	+112.2	-	+41.8	+22.6	+17.8
Mg <sup>2+</sup>	-12.6	-160.0	-185.6	-213.2	+2.3	-25.3	-90.9	-91.2
Ca <sup>2+</sup>	+11.5	-81.3	-103.1	-119.7	-16.7	-13.1	-19.2	-18.0
Al <sup>3+</sup>	-27	-329	-368	-385	-	-	-	-350

# Enthalpy of Solution

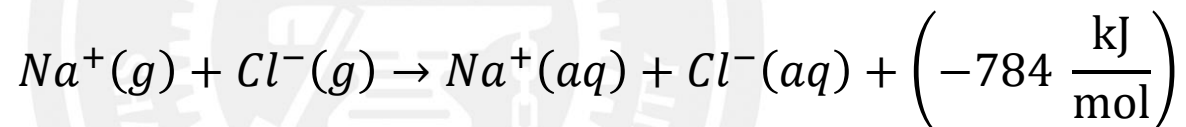


The first step sublimates solid ions to gaseous ions. This is a highly endothermic process and is known as **lattice enthalpy**,  $\Delta H_L$ :

$$\Delta H_{L,NaCl} = 787 \frac{\text{kJ}}{\text{mol}}$$



In the second step, gaseous ions plunge into water forming the final solution. This is known as the **enthalpy of hydration**,  $\Delta H_{hyd}$ , and for NaCl:



$$\Delta H_{sol} = \Delta H_L + \Delta H_{hyd}$$

$$\Delta H_{sol,NaCl} = 787 \frac{\text{kJ}}{\text{mol}} + \left(-784 \frac{\text{kJ}}{\text{mol}}\right) = +3 \frac{\text{kJ}}{\text{mol}} \text{ (endothermic)}$$

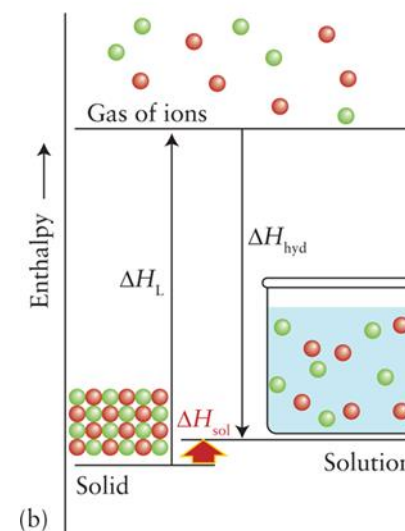
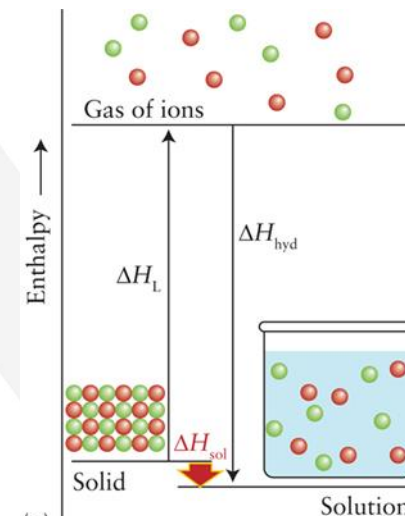


Figure 5D.10  
Atkins, *Chemical Principles: The Quest for Insight*,  
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# Enthalpy of Solution: Factors



$$\Delta H_{sol} = \Delta H_L + \Delta H_{hyd}$$

$\Delta H_L$ : endothermic, positive

$\Delta H_{hyd}$ : usually exothermic, negative

**High charge** and **small ionic radius** contribute to **high** lattice enthalpy ( $\Delta H_L$ ).

*However, often these can be the same properties* that relate to **low** enthalpy of hydration ( $\Delta H_{hyd}$ ).

Therefore it is *very difficult* to make reliable predictions and instead rationalize what is observed.



# Gibbs Free Energy of Solution

$$\Delta H_{sol} = \Delta H_L + \Delta H_{hyd}$$

A negative enthalpy,  $\Delta H_{sol} < 0$ , is an **energy releasing** process.

Solvation leads to an increase in entropy.  
 $\Delta S > 0$

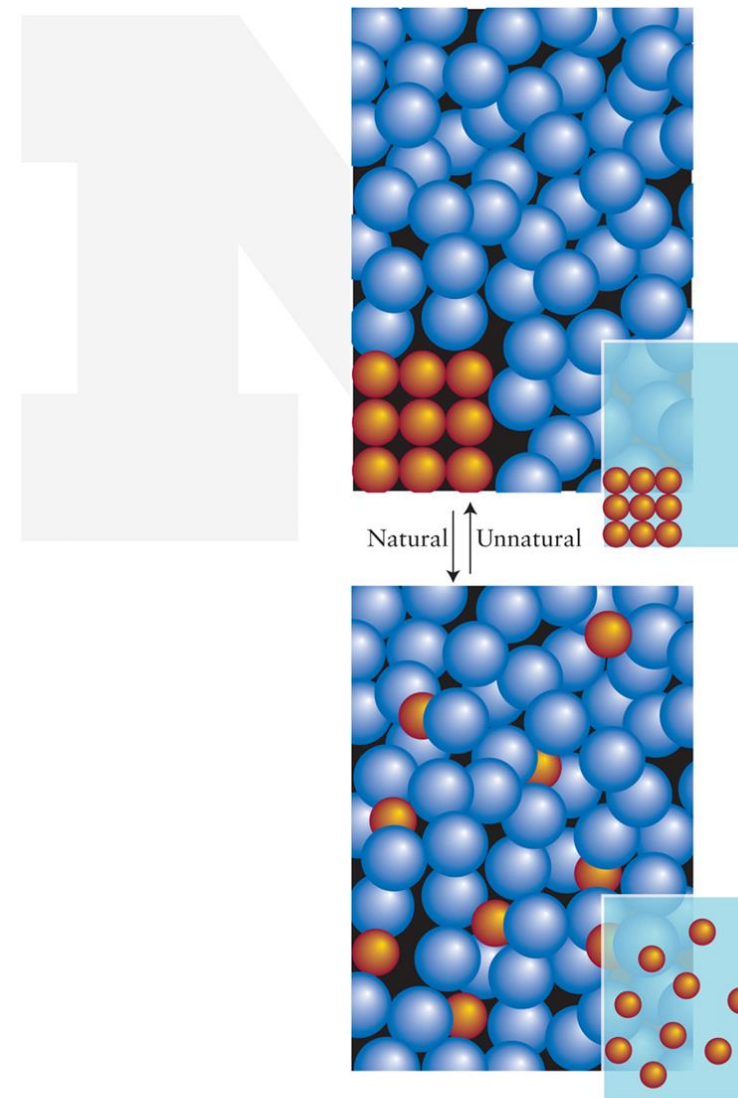


Figure 5D.11

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The Gibbs Free Energy of Solution:

**An Increase in  $\Delta S$  (total)**

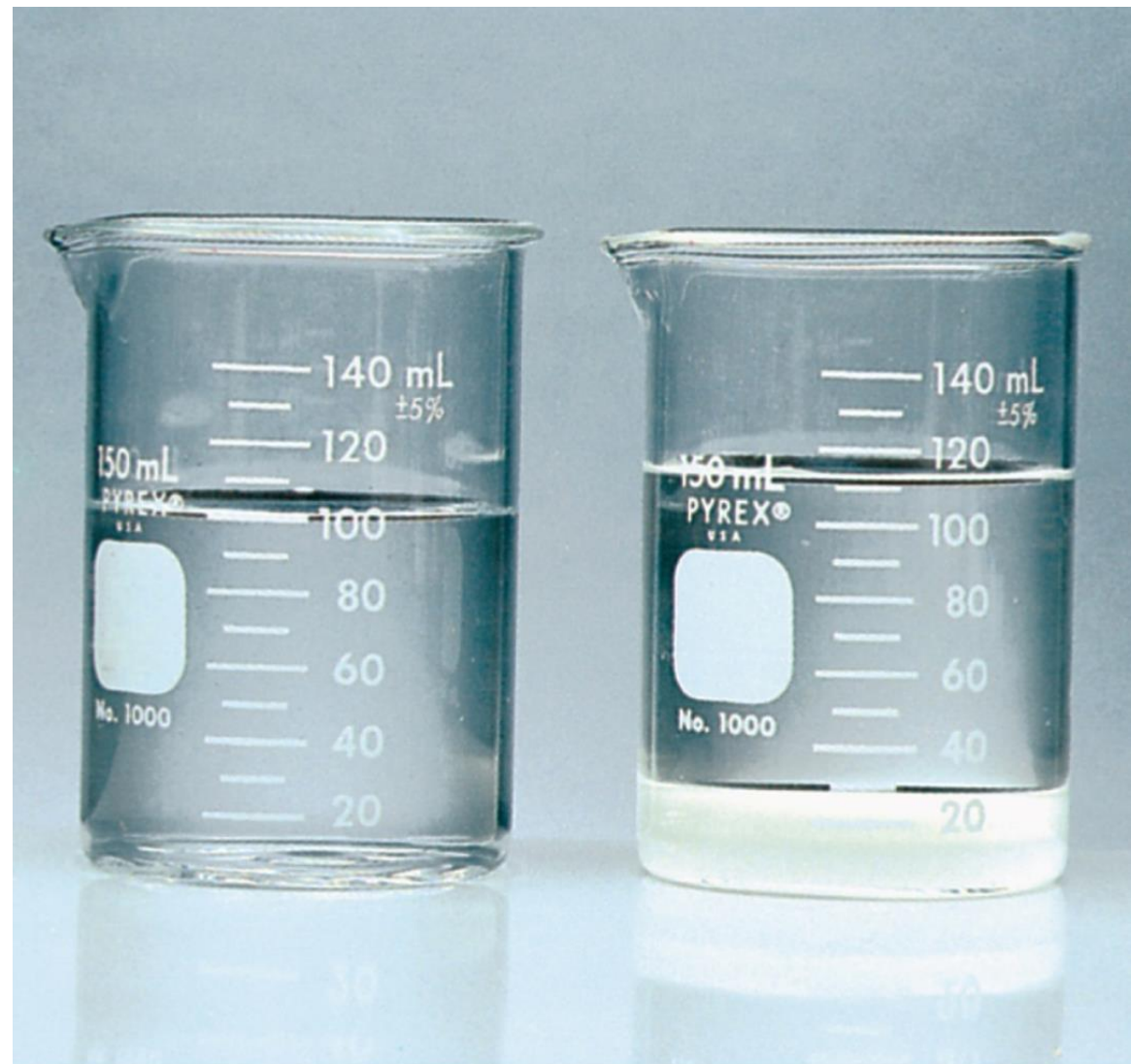
A spontaneous change (at constant temperature and pressure) is the Gibbs free energy,  $\Delta G = \Delta H - T \cdot \Delta S$ .

**Dissolving a solid increases the disorder of a system**, so we expect  $\Delta S$  to increase or be positive.

Forming a solution (solute and solvent)

“Free” water molecules pull crystals of glucose into the solution.

Both stirring and heating increase the solubility process.



**Figure 5D.2**  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman photo by Ken Karp.

# Solubility Limits

Glucose is **unsaturated** at 20 g of glucose per 100 mL of water.

Beyond this point is a **saturated** solution. Excess glucose molecules will fall out of solution.

*“If you are not part of the solution,  
you are part of the precipitate.”*

-Chemist's Proverb

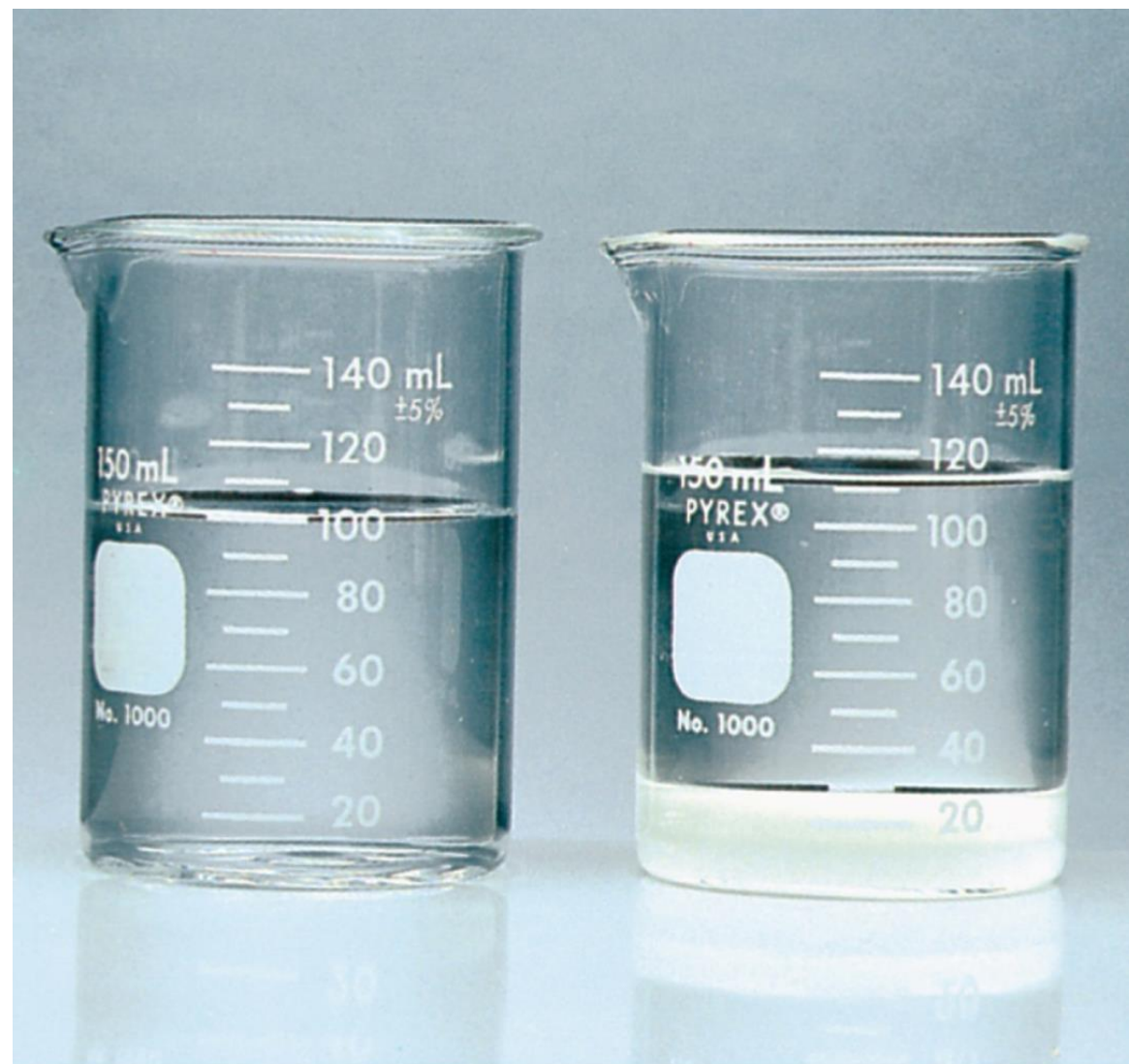


Figure 5D.2

Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman photo by Ken Karp.

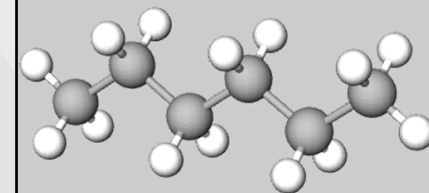
# Like Dissolves Like

A good guide is:

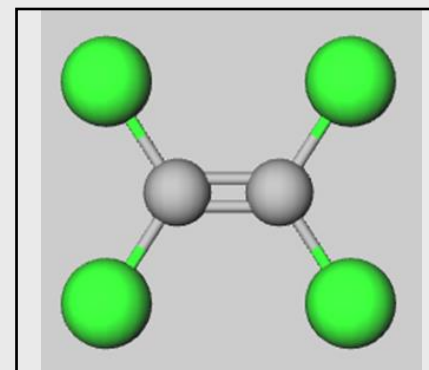
**Like dissolves like.**

Water (polar) can dissolve other polar and ionic compounds.

Hexane and tetrachloroethene (nonpolar),  $\text{Cl}_2\text{C}=\text{CCl}_2$ , dry-cleaning solvents, interact with other nonpolar compounds through London forces.



*n*-Hexane  
 $\text{C}_6\text{H}_{14}$



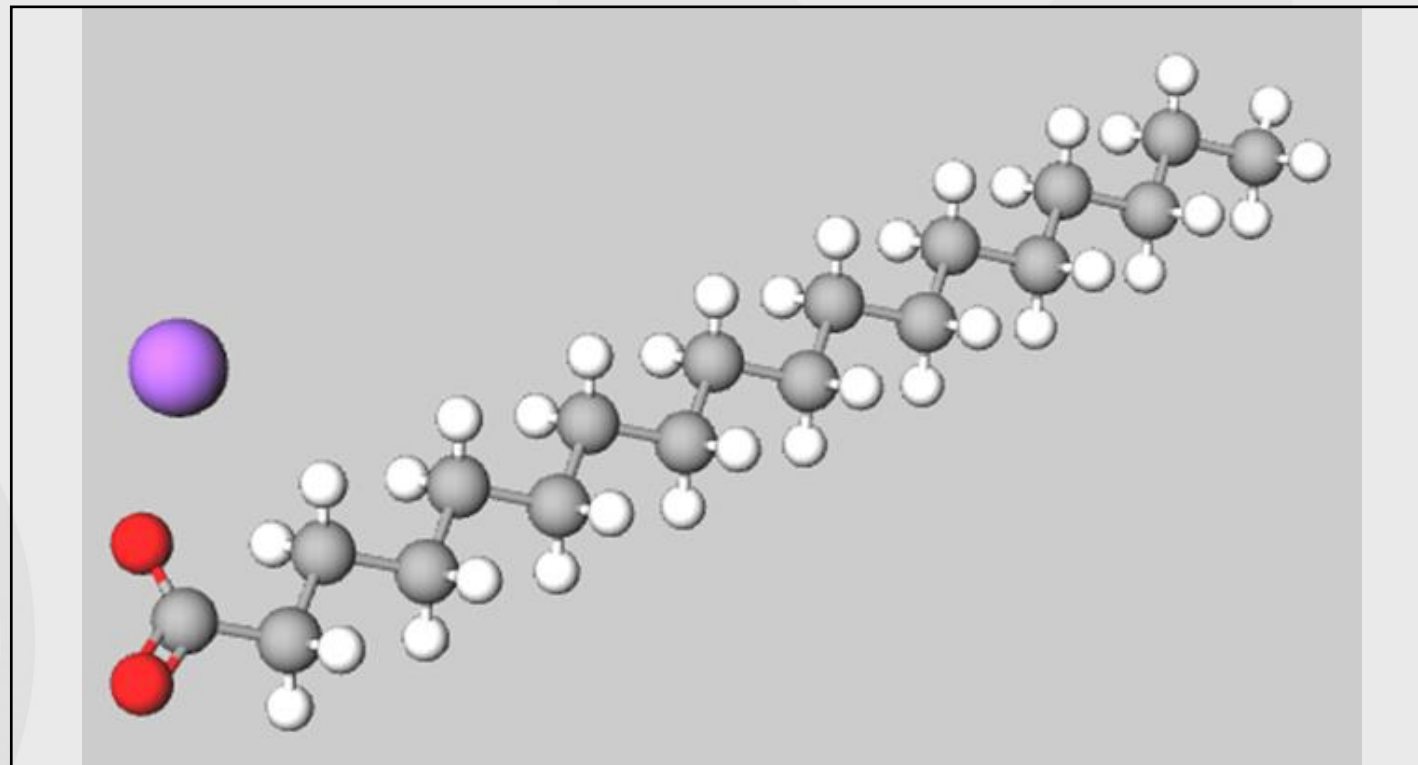
Tetrachloroethene  
 $\text{C}_2\text{Cl}_4$



# Solubility: Like Dissolves Like

The cleaning action of soaps and detergents relies on the like-dissolves-like rule.

Soaps are long-chain carboxylic acids, including sodium stearate.



Sodium stearate  
 $NaCH_3(CH_2)_{16}CO_2$

# Solubility: Like Dissolves Like

Soap has polar **head** carboxylates ( $\text{CO}_2^-$ ) attached to a nonpolar hydrocarbon **tail**.

The **hydrophobic** nonpolar hydrocarbon tails sink into blobs of grease.

The **hydrophilic** head encases the grease into a **micelle**, letting water wash the grease away.

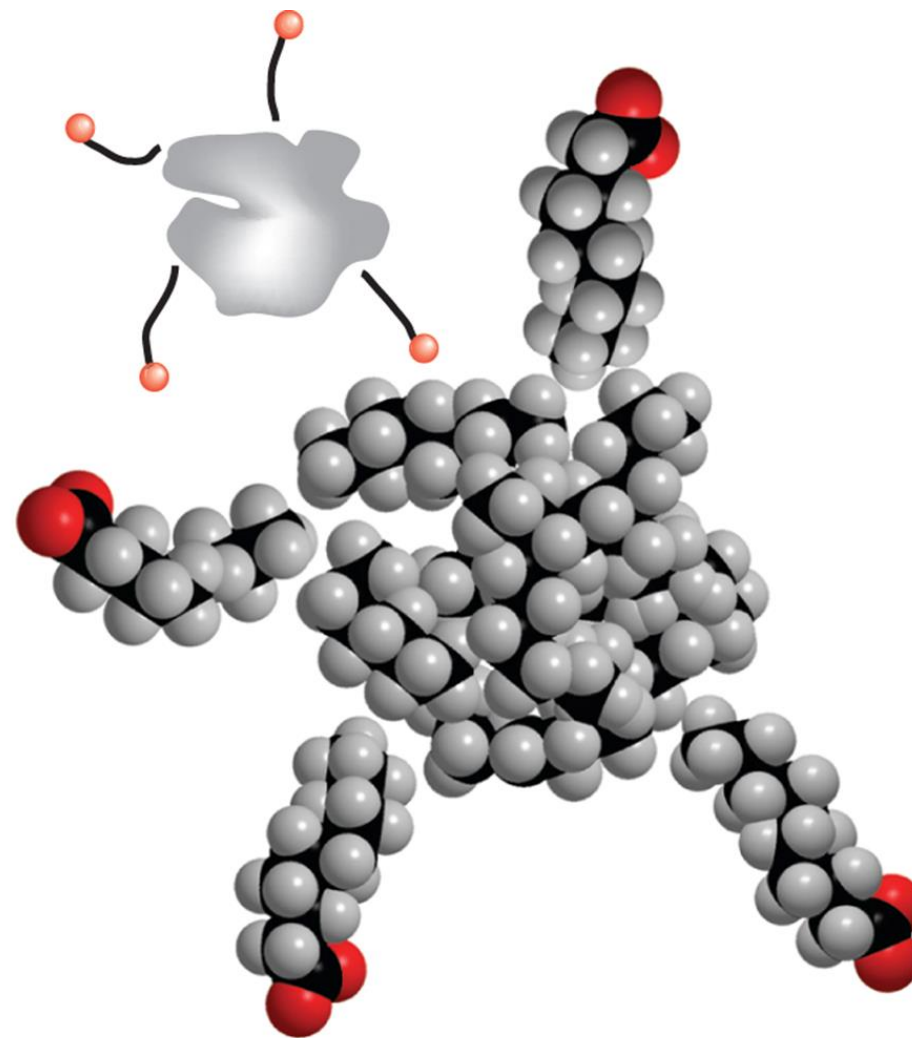


Figure 5D.7

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# Temperature and Solubility



**Solids** dissolve more quickly (are more soluble) at higher temperatures than at low ones, but which does not necessarily hold for solubility.

Higher temperature means **faster** solvation, **not more** solvation.

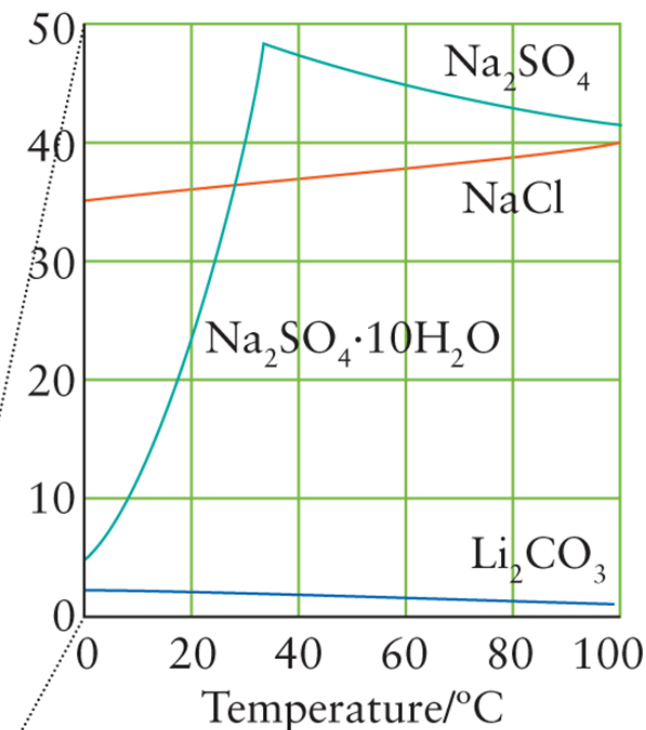
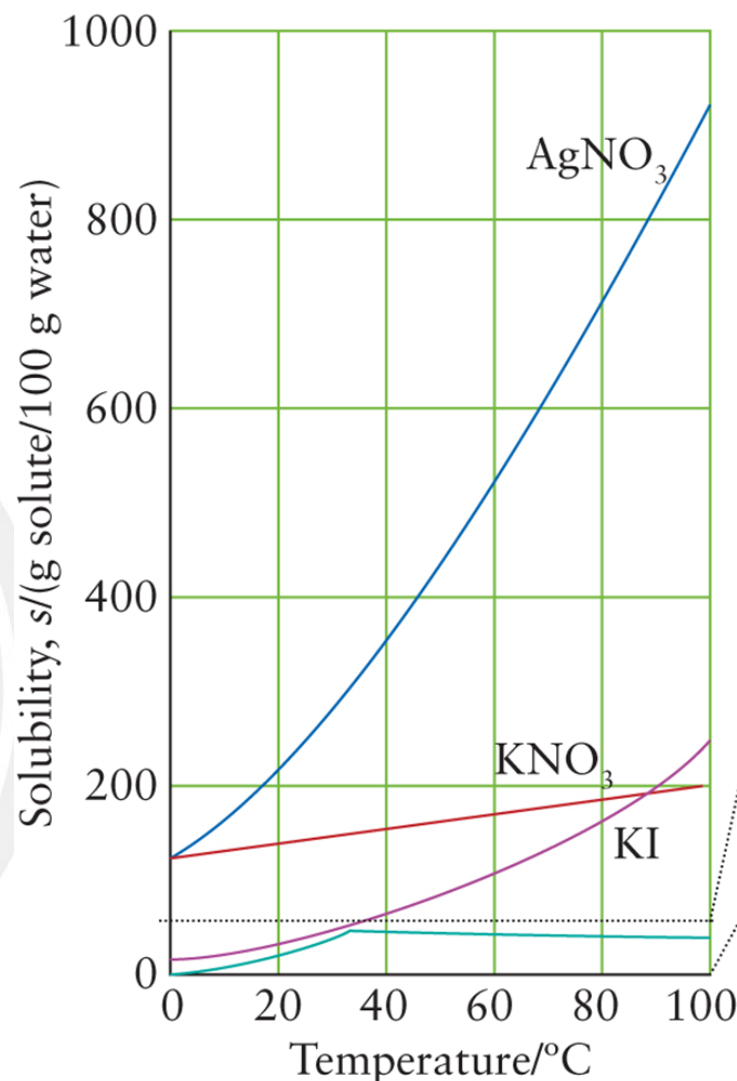


Figure 5D.9

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The seal of Shanghai Jiao Tong University, featuring a circular emblem with a building, the year '1896', and the text 'SHANGHAI JIAO TONG UNIVERSITY'.

# Properties of Dilute Solutions

A large, light gray, stylized letter 'M' in the background.

Properties that **depend on the numbers** of solute and solvent molecules and not on chemical identity are called **colligative properties**.

Four colligative properties of major importance are:

1. lowering of the vapour pressure
2. raising of boiling points
3. lowering of freezing points
4. osmosis

Extensive properties depend on the quantity of matter (e.g, volume, mass), whereas intensive properties are independent of the quantity of matter (e.g., density, temperature). **Colligative** is a new, third category.

Colligative properties are measured using either **mole fraction** or **molality**.

Both indicate the relative amounts of solute and solvent molecules (not mass or volume).

**Mole fraction:**

$$\chi_A = \frac{n_A}{n_A + n_B + \cdots}$$

$$\chi_A + \chi_B + \cdots = 1$$

(Also covered in Chapter 5, under Dalton's Law)

The molality of a solute is the amount of solute species (in moles) divided by the mass of the solvent (in kilograms):

**Molality:**

$$m = \frac{\text{amount of solute}}{\text{mass of solvent}} = \frac{n_{\text{solute}}}{m_{\text{solvent}}} \left[ \frac{\text{mol}}{\text{kg}} \right]$$

Molality is *independent of temperature* (not true for molarity).

The unit of *molality* is  $\text{mol} \cdot \text{kg}^{-1}$  and denoted as “***m***”. For example, a 1.0 *m*  $\text{NiSO}_4(aq)$  would read as 1.0 **molal** and it is exactly 1 mol  $\text{NiSO}_4$  dissolved in 1 kg of water.

# Example



What is the molality of NaCl in a solution prepared by dissolving 10.5 g of sodium chloride in 250 g of water?

$$M_{NaCl} = 58.44 \frac{\text{g}}{\text{mol}}$$

$$m = \frac{n_{\text{solute}}}{m_{\text{solvent}}} \left[ \frac{\text{mol}}{\text{kg}} \right] = \frac{\frac{m_{NaCl}}{M_{NaCl}}}{m_{H_2O}}$$

$$m = \frac{\frac{10.5 \text{ g}}{58.44 \frac{\text{g}}{\text{mol}}}}{0.250 \text{ kg}} = 0.719 \frac{\text{mol}}{\text{kg}} = 0.719 m$$

Mole fraction:

$$\chi_{solute} = \frac{n_{solute}}{n_{solute} + n_{solvent}} \text{ or } \chi_{solvent} = \frac{n_{solvent}}{n_{solute} + n_{solvent}}$$

$$\chi_{solute} + \chi_{solvent} = 1$$

Solvent mass from mole fraction:

$$m_{solvent} = n_{solvent} \cdot M_{solvent} = (1 - \chi_{solute}) \cdot M_{solvent}$$

Molality from molarity:

$$\frac{n_{solute}}{m_{solvent}} = \frac{c_{solution} \cdot V_{solution}}{m_{solution} - (c_{solution} \cdot V_{solution} \cdot M_{solute})}$$



# Example



What is the molality of benzene,  $\text{C}_6\text{H}_6$ , dissolved in toluene,  $\text{C}_6\text{H}_5\text{CH}_3$ , in a solution for which the mole fraction of benzene is 0.150?

$$M_{\text{benzene}} = 78.11 \frac{\text{g}}{\text{mol}}, M_{\text{toluene}} = 92.13 \frac{\text{g}}{\text{mol}}$$

$$m = \frac{n_{\text{solute}}}{m_{\text{solvent}}} = \frac{n_{\text{benzene}}}{m_{\text{toluene}}}$$

$$m = \frac{n_{\text{benzene}}}{m_{\text{toluene}}} = \frac{n_{\text{benzene}}}{n_{\text{toluene}} \cdot M_{\text{toluene}}} = \frac{\chi_{\text{benzene}} \cdot (n_{\text{benzene}} + n_{\text{toluene}})}{\chi_{\text{toluene}} \cdot (n_{\text{benzene}} + n_{\text{toluene}}) \cdot M_{\text{toluene}}}$$

$$m = \frac{\chi_{\text{benzene}}}{(1 - \chi_{\text{benzene}}) \cdot M_{\text{toluene}}} = \frac{0.150}{(1 - 0.150) \times 0.09213 \frac{\text{kg}}{\text{mol}}} = 1.92 \frac{\text{mol}}{\text{kg}}$$

# Example



Find the molality of sucrose,  $C_{12}H_{22}O_{11}$ , in 1.06 M  $C_{12}H_{22}O_{11}(aq)$ , which is known to have density  $1.14 \text{ g}\cdot\text{mL}^{-1}$ .

$$M_{C_{12}H_{22}O_{11}} = 342.3 \frac{\text{g}}{\text{mol}}$$

$$m = \frac{n_{\text{solute}}}{m_{\text{solvent}}} = \frac{c_{\text{solution}} \cdot V_{\text{solution}}}{m_{\text{solution}} - (c_{\text{solution}} \cdot V_{\text{solution}} \cdot M_{\text{solute}})}$$

$$m = \frac{c_{\text{solution}} \cdot V_{\text{solution}}}{V_{\text{solution}} \cdot \rho_{\text{solution}} - (c_{\text{solution}} \cdot V_{\text{solution}} \cdot M_{C_{12}H_{22}O_{11}})}$$

Assume  $V_{\text{solution}} = 1 \text{ L}$ :

$$m = \frac{1.06 \frac{\text{mol}}{\text{L}} \times 1 \text{ L}}{1 \text{ L} \times 1.14 \frac{\text{kg}}{\text{L}} - \left(1.06 \frac{\text{mol}}{\text{L}} \times 1 \text{ L} \times 0.3423 \frac{\text{kg}}{\text{mol}}\right)} = 1.36 \frac{\text{mol}}{\text{kg}}$$

A **nonvolatile solute** lowers the vapour pressure of the solvent, therefore increasing the boiling point and therefore it is called **boiling-point elevation**.

The **effect of the solute** on the **entropy** of the solvent increases more than in the pure solvent, thus the boiling point is higher in the presence of the solute.

# Colligative Effects on $T_m$ and $T_b$



**The increase** in boiling temperature is usually quite small and is of **little practical importance in science**.

A 0.1 m aqueous sucrose solution, for instance, boils at 100.05 °C.

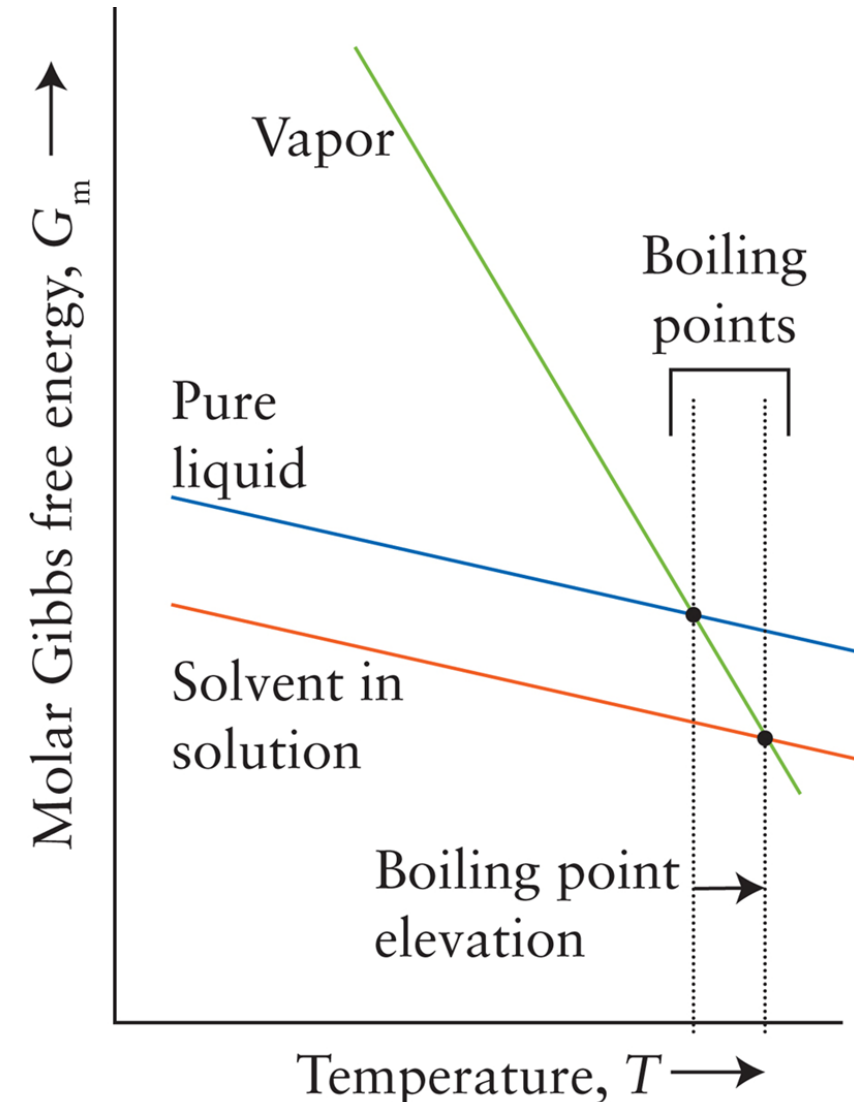


Figure 5F.1

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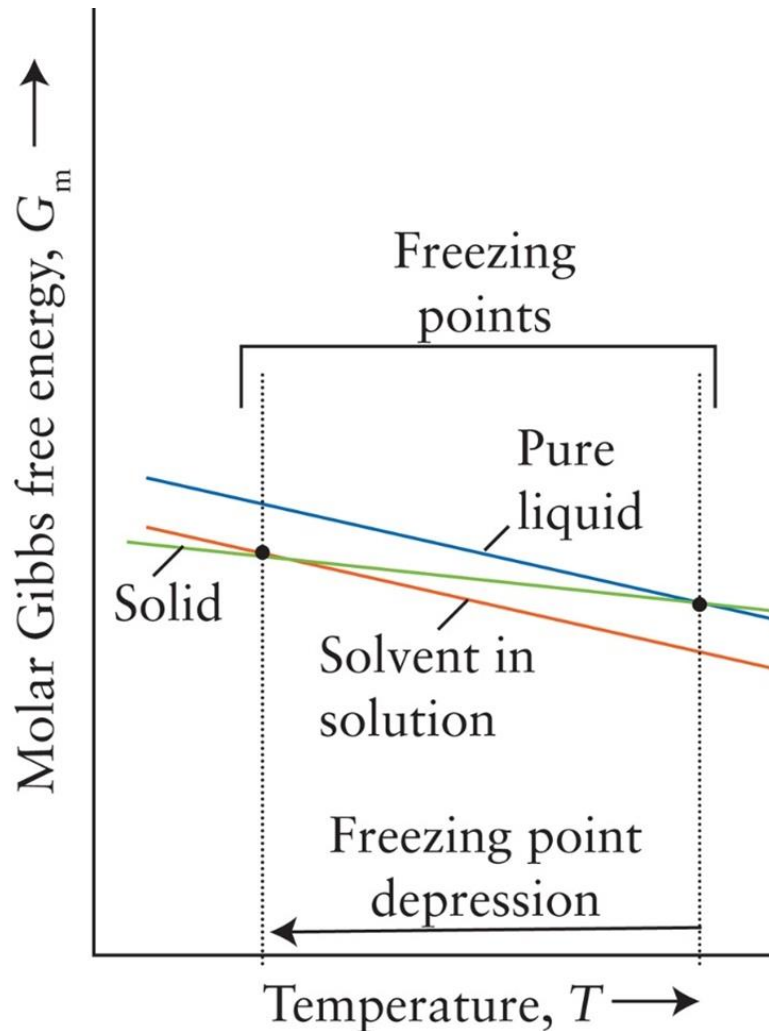


Figure 5F.2  
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**Freezing-point depression** is more significant. An added solute lowers of the freezing point of a solvent.

Seawater freezes about 1 °C **lower** than fresh water.

**Salting** walkways and roads lowers the water's freezing point, thus melting it.

The melting point is also a method for determining the **purity of a solid**.

**Freezing-point depression** =  $k_f \times \text{molality}$ , temperature decreases.

**Boiling-point elevation** =  $k_b \times \text{molality}$ , temperature increases.

Solvent	$T_m / ^\circ\text{C}$	$k_f / \text{K}\cdot\text{kg}\cdot\text{mol}^{-1}$	$T_b / ^\circ\text{C}$	$k_b / \text{K}\cdot\text{kg}\cdot\text{mol}^{-1}$
Acetone	-95.35	2.40	56.2	1.71
Benzene	5.5	5.12	80.1	2.53
Camphor	179.8	39.7	204	5.61
Carbon tetrachloride	-23	29.8	76.5	4.95
Cyclohexane	6.5	20.1	80.7	2.79
Naphthalene	80.5	6.94	217.7	5.80
Phenol	43	7.27	182	3.04
Water	0	1.86	100.0	0.51



# Colligative Effects on $T_m$ and $T_b$



The effect is small. For a 0.1 m  $C_{12}H_{22}O_{11}(aq)$  (sucrose) solution:

$$\text{Freezing - point depression} = k_f \cdot \text{molality} = 1.86 \frac{\text{K} \cdot \text{kg}}{\text{mol}} \times 0.1 \frac{\text{mol}}{\text{kg}} = 0.2 \text{ K}$$

Therefore, water would freeze at  $-0.2^\circ\text{C}$ .

Solvent	$T_m / ^\circ\text{C}$	$k_f / \text{K} \cdot \text{kg} \cdot \text{mol}^{-1}$	$T_b / ^\circ\text{C}$	$k_b / \text{K} \cdot \text{kg} \cdot \text{mol}^{-1}$
Acetone	-95.35	2.40	56.2	1.71
Benzene	5.5	5.12	80.1	2.53
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Phenol	43	7.27	182	3.04
Water	0	1.86	100.0	0.51

# Example



Determine at what temperature a  $0.050 \text{ mol}\cdot\text{kg}^{-1}$  solution of the insecticide malathion,  $\text{C}_{10}\text{H}_{19}\text{O}_6\text{PS}_2$ , in camphor will freeze.

$$T_{m,\text{camphor}} = 179.8 \text{ }^\circ\text{C}, k_{f,\text{camphor}} = 39.7 \frac{\text{K}\cdot\text{kg}}{\text{mol}}$$

$$\text{Freezing} - \text{point depression} = k_f \cdot \text{molality} = 39.7 \frac{\text{K}\cdot\text{kg}}{\text{mol}} \times 0.050 \frac{\text{mol}}{\text{kg}} = 1.99 \text{ K}$$

But this is the freezing-point depression, not the freezing point of the solution.

$$T_{m,\text{solution}} = T_{m,\text{camphor}} - \text{Freezing} - \text{point depression} = 179.8 \text{ }^\circ\text{C} - 1.99 \text{ }^\circ\text{C} = 177.8 \text{ }^\circ\text{C}$$

In an *electrolyte solution*, each formula unit contributes two or more ions. For example, sodium chloride gives  $\text{Na}^+$  and  $\text{Cl}^-$  ions and both ions contribute to the depression of the freezing point.

$$\text{Freezing} - \text{point depression} = i \cdot k_f \cdot \text{molality}$$

The van't Hoff  $i$  factor, is determined experimentally.

In very dilute solution  $\left(c < 0.001 \frac{\text{mol}}{\text{L}}\right)$ , where all ions are independent,  $i = 2$  for  $MX$  salts such as  $\text{NaCl}$ , and for  $MX_2$  salts such as  $\text{CaCl}_2$ ,  $i = 3$ .

# Short Quiz



Of the following four materials, which has the lowest freezing point and the highest boiling point in water?

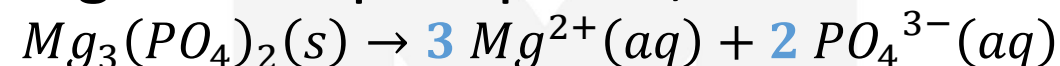
A. 1.0 *mm* magnesium phosphate  
 $\text{Mg}_3(\text{PO}_4)_2$

B. 1.0 *mm* sodium chloride  $\text{NaCl}$

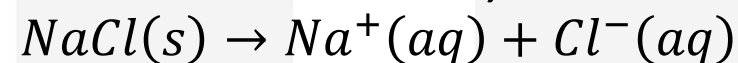
C. 1.0 *mm* calcium chloride  $\text{CaCl}_2$

D. 1.0 *mm* aluminium nitrate  
 $\text{Al}(\text{NO}_3)_3$

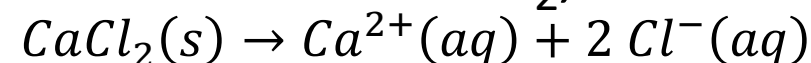
Magnesium phosphate,  $i = 5$



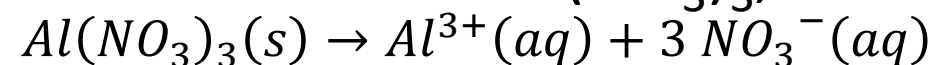
Sodium chloride:  $\text{NaCl}$ ,  $i = 2$



Calcium Chloride:  $\text{CaCl}_2$ ,  $i = 3$



Aluminium nitrate:  $\text{Al}(\text{NO}_3)_3$ ,  $i = 4$



# Example



The addition of 0.24 g of sulfur to 100 g of the solvent carbon tetrachloride lowers the solvent's freezing point by 0.28 °C. What is the molar mass and molecular formula of sulfur?

$$M_S = 32.1 \frac{\text{g}}{\text{mol}}, k_f = 29.8 \frac{\text{K} \cdot \text{kg}}{\text{mol}}, i = 1 \text{ (nonelectrolyte)}$$

$$\text{Freezing - point depression} = i \cdot k_f \cdot \text{molality}$$

$$\text{molality} = \frac{\text{freezing - point depression}}{i \cdot k_f} = \frac{n_{\text{solute}}}{m_{\text{solvent}}}$$

$$M_{\text{solute}} = \frac{m_{\text{solute}}}{n_{\text{solute}}} = \frac{m_{\text{solute}}}{\frac{\text{freezing - point depression} \cdot m_{\text{solvent}}}{i \cdot k_f}} = \frac{0.24 \text{ g}}{\frac{0.28 \text{ K} \times 0.100 \text{ kg}}{1 \times 29.8 \frac{\text{K} \cdot \text{kg}}{\text{mol}}}} = 260 \frac{\text{g}}{\text{mol}}$$

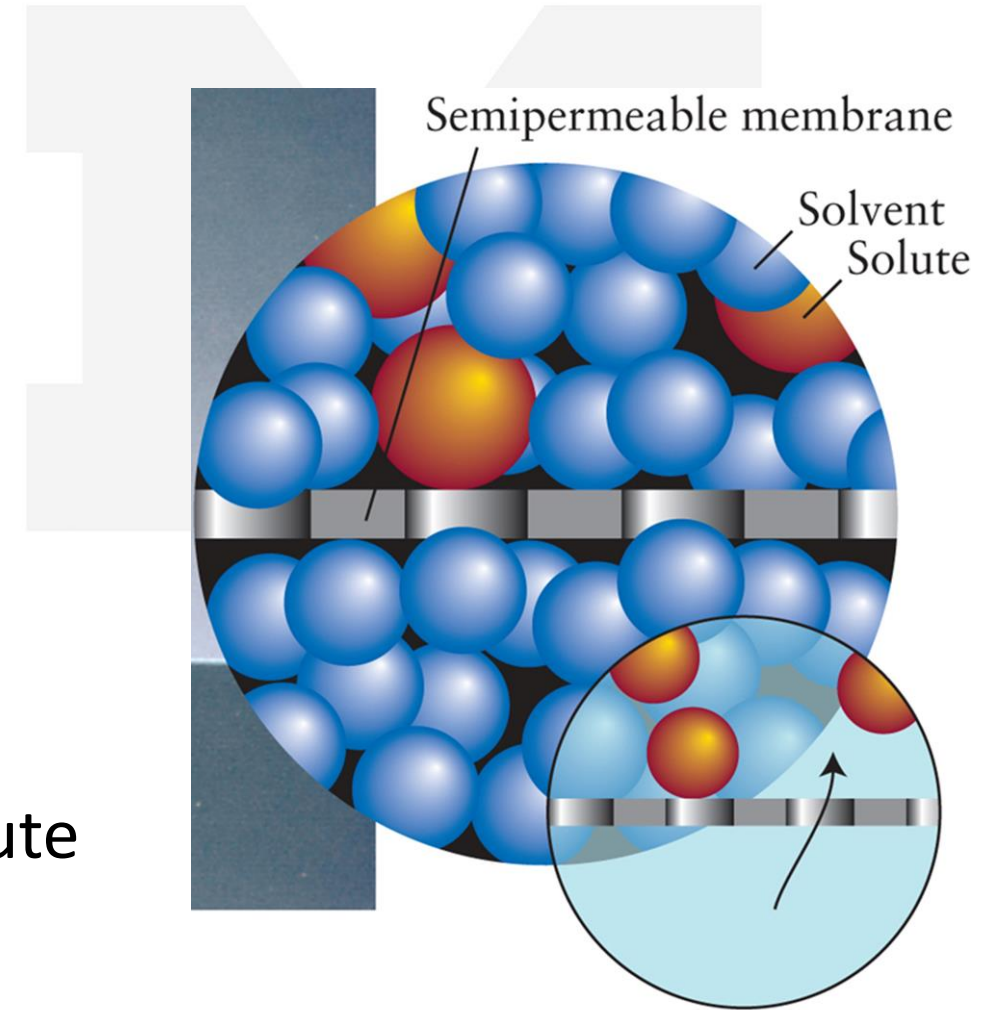
$$\text{Molecular formula} = \frac{M_{\text{solute}}}{M_S} = \frac{260 \frac{\text{g}}{\text{mol}}}{32.1 \frac{\text{g}}{\text{mol}}} = 8, \text{ therefore: } \text{S}_8$$

# Osmosis

Osmosis is the flow of solvent through a membrane into a more concentrated solution.

The membrane permits only certain types of molecules or ions to pass through.

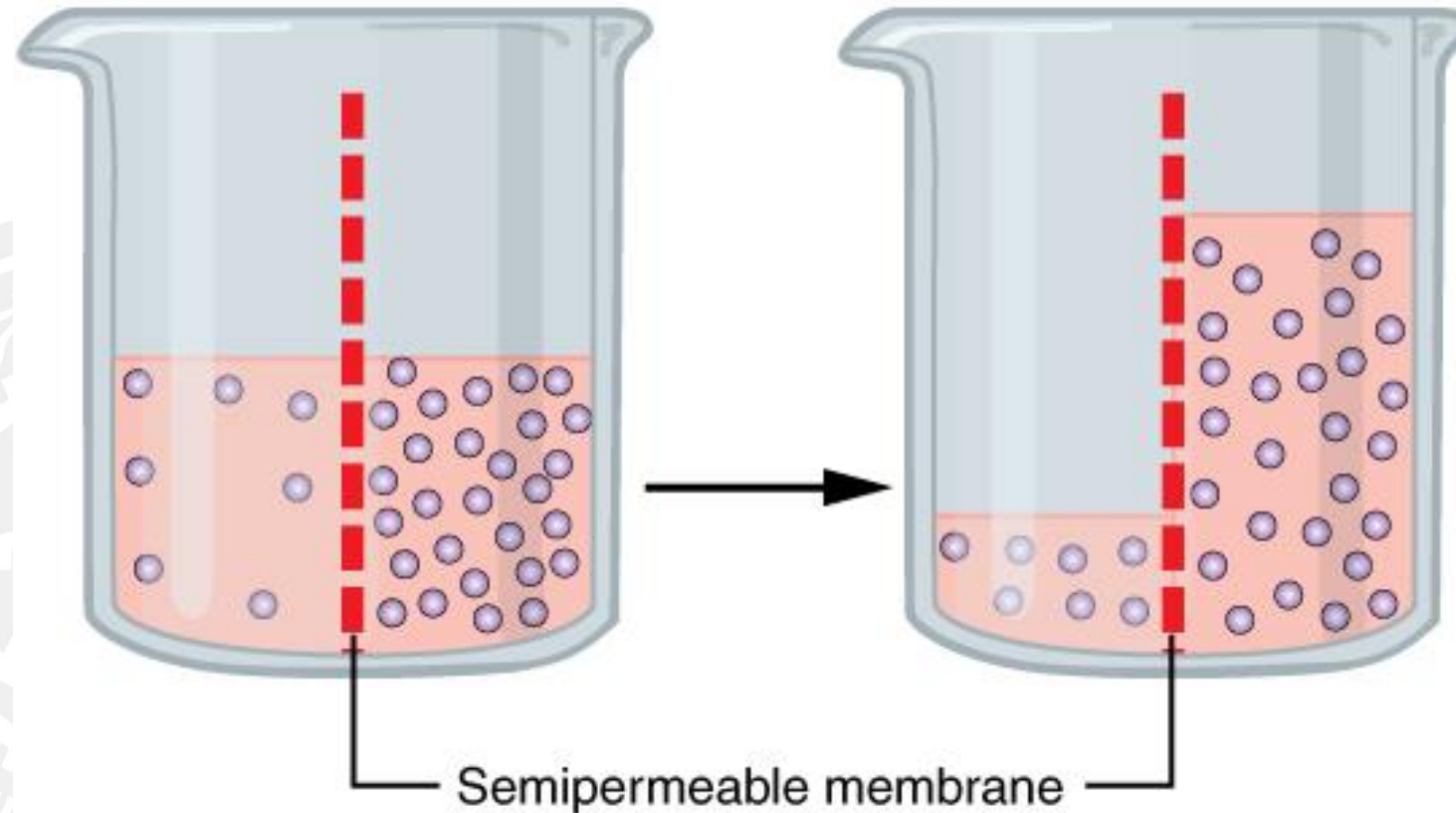
Cellulose acetate, for instance, *allows* water molecules to pass through it, but *not* bulky solute molecules or ions coated with hydrated water molecules.





# Osmosis

A net movement of solvent → equal concentration of solutions



The pressure needed to stop the flow of solvent is called the **osmotic pressure**,  $\Pi$

# Osmosis in Biology



Biological cell walls act as **semipermeable membranes** that **allow water, small molecules**, and hydrated ions to pass, yet **block the passage** of the enzymes and proteins.

*Water passes into the more concentrated solution* in the interior of the cell, carrying small nutrient molecules with it.

This influx of water also keeps the cell **turgid** (swollen). When the water supply is cut off, the turgidity is lost, and the cell becomes dehydrated.

**Salted meat is preserved** from bacterial attack by osmosis; high concentrated salt solution **dehydrates** and kills the bacteria by causing water to flow out of them.

# Osmosis

Osmosis is a thermodynamic process.

$$G = H - TS$$

Solvent flows until the molar Gibbs free energy of the solvent is the same on each side of the membrane.

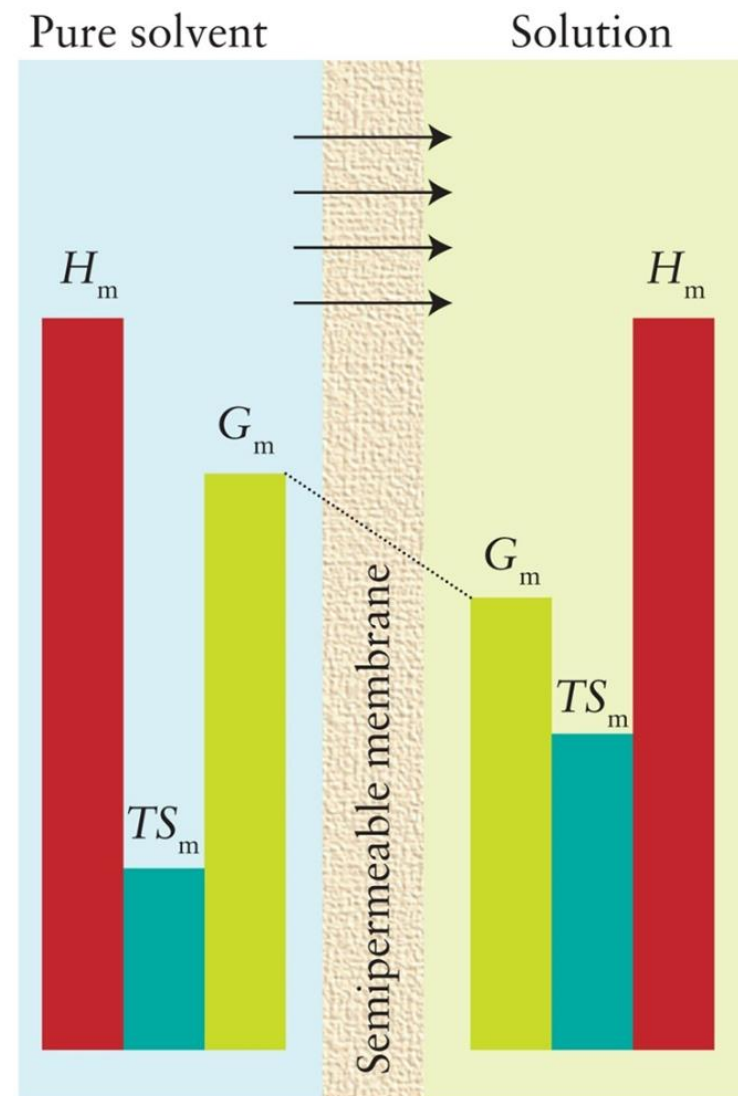


Figure 5F.5

Atkins, *Chemical Principles: The Quest for Insight*, 7e

W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

The van 't Hoff  $i$  factor also appears in osmotic pressure:

$$\Pi = i \cdot RT \cdot c$$

$c$ : concentration or molarity

$R$ : gas constant

$T$ : temperature

Osmometry is the technique used to determine the molar mass of a solute from osmotic pressure measurements.

# Example



The osmotic pressure due to 2.20 g of polyethylene (PE) dissolved in enough benzene to produce 100 mL of solution was  $1.10 \times 10^{-2}$  atm at 25 °C. Calculate the average molar mass of the polymer, which is a nonelectrolyte ( $i = 1$ ).

$$\Pi = i \cdot RT \cdot c = i \cdot RT \cdot \frac{n_{\text{solute}}}{V_{\text{solution}}} = i \cdot RT \cdot \frac{\frac{m_{\text{solute}}}{M_{\text{solute}}}}{V_{\text{solution}}}$$

$$M_{\text{solute}} = \frac{m_{\text{solute}} \cdot i \cdot RT}{\Pi \cdot V_{\text{solution}}}$$

$$M_{PE} = \frac{2.20 \text{ g} \times 1 \times 8.314 \frac{\text{N} \cdot \text{m}}{\text{mol} \cdot \text{K}} \times (273.15 + 25) \text{K}}{1.10 \times 10^{-2} \text{ atm} \times 101325 \frac{\text{N} \cdot \text{m}}{\text{m}^3 \cdot \text{atm}} \times 0.100 \times 10^{-3} \text{ m}^3} = 4.89 \times 10^4 \frac{\text{g}}{\text{mol}}$$