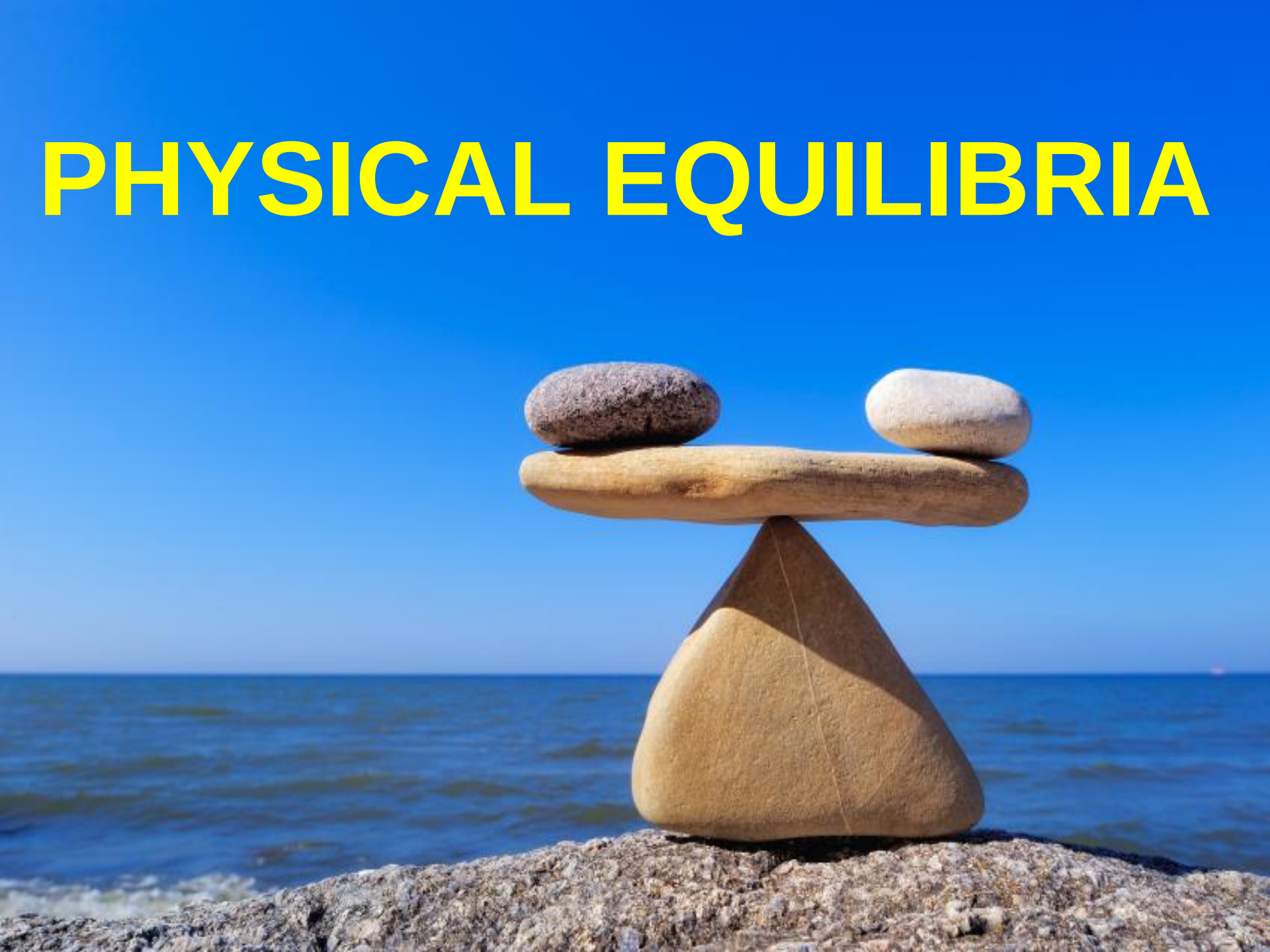
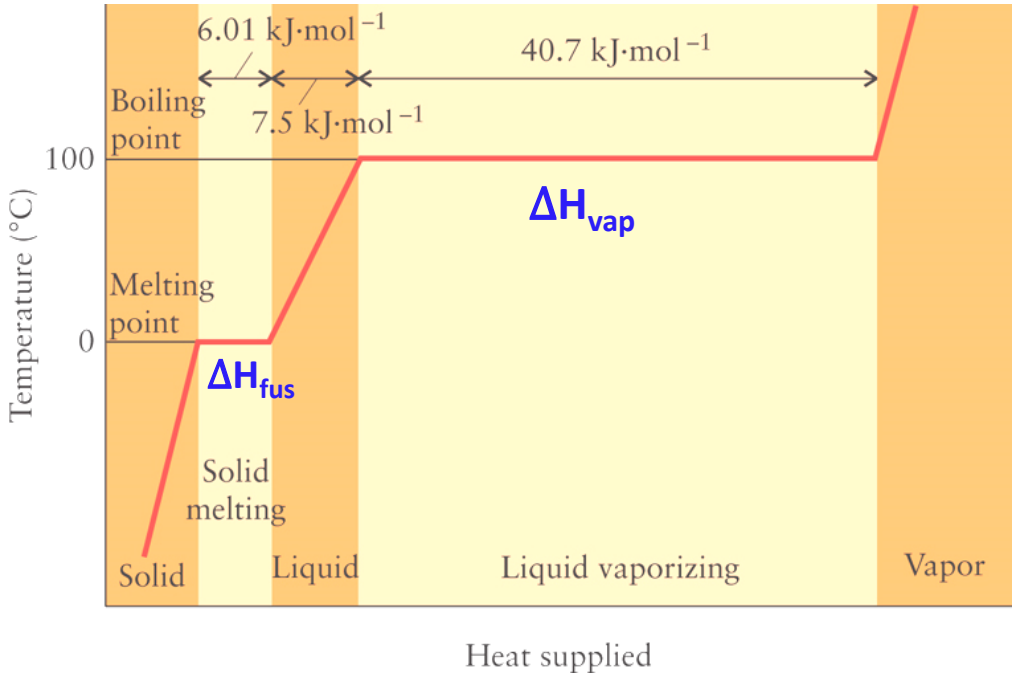
PHYSICAL EQUILIBRIA



Phase Changes

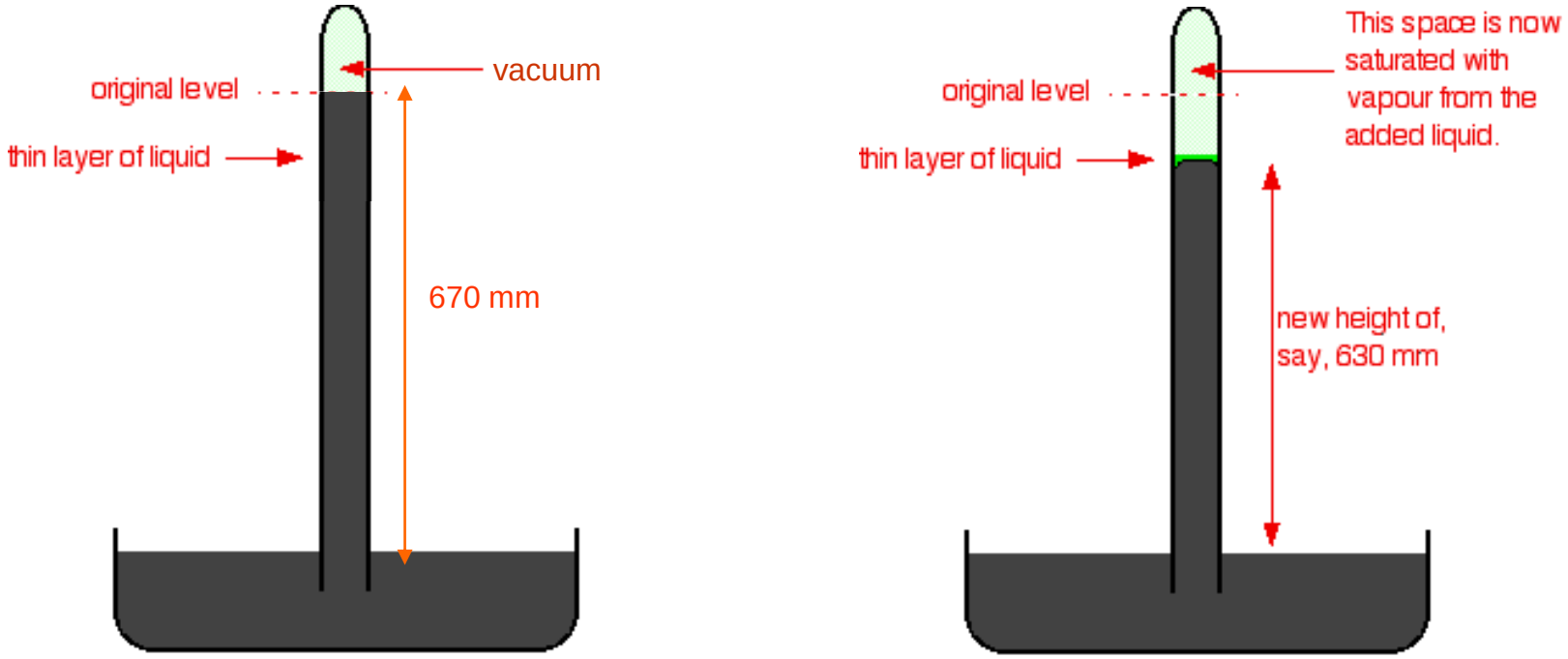
A **phase change** occurs when converting one phase into another.

phase changes, at constant temperature, are an equilibrium process, **ΔG = 0**.



Vapor Pressure

Vapor pressure: the pressure of a gas in equilibrium with its liquid form in a closed container.



Measuring vapor pressure of liquids

Vapor Pressure

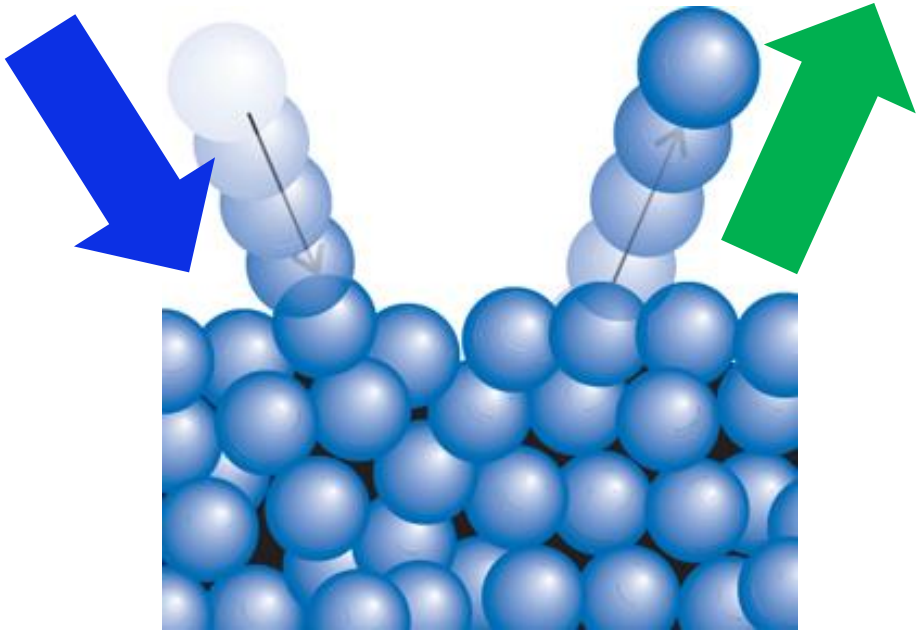
A volatile substance has a vapor pressures at *ordinary temperatures*.

Methanol (vapor pressure 98 Torr at 20°C) is highly volatile.

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

When a solid vaporizes, the process is called "**sublimation**“

Vapor Pressure



Evaporation takes place at the surface because molecules are bound to fewer neighbors.

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

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

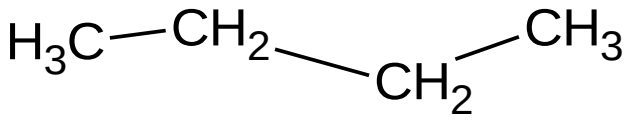
rate of evaporation = *rate* of condensation

Volatility & Intermolecular Forces

The strength of the intermolecular forces determines it's vapor pressure.

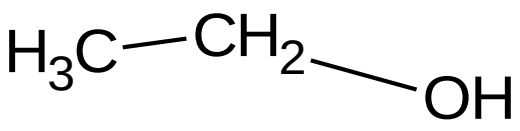
Liquids with **weak intermolecular forces** have the **highest vapor pressure**.

Butane 220 kPa

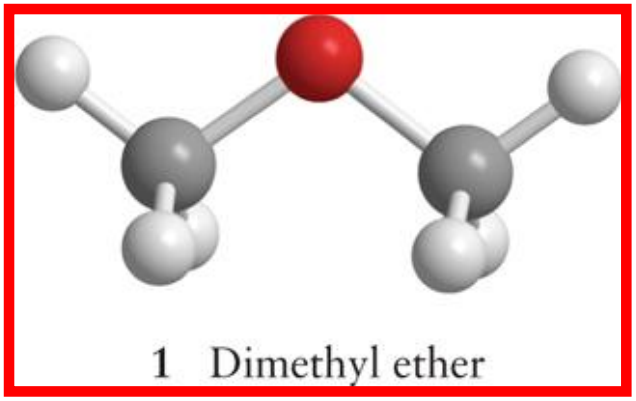


Liquids with **strong intermolecular forces**, ones capable of **forming hydrogen bonds** have the **lowest vapor pressure**.

Propanol: 2.4 kPa



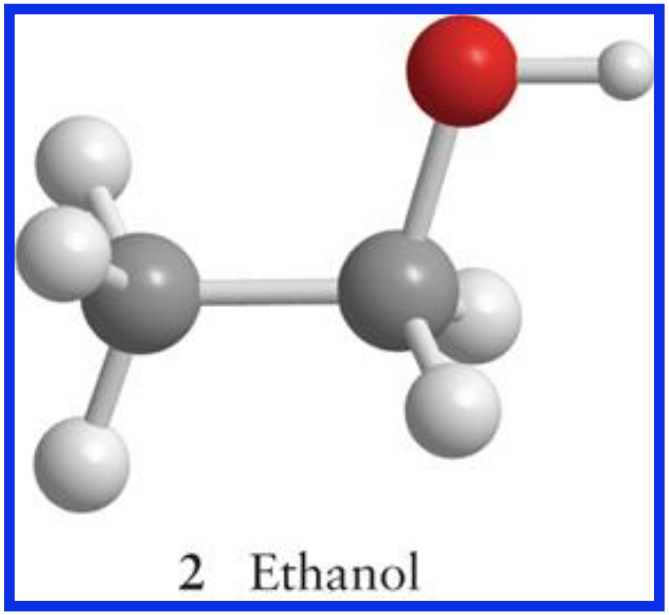
Volatility & Intermolecular Forces



1 Dimethyl ether

>580 kPa

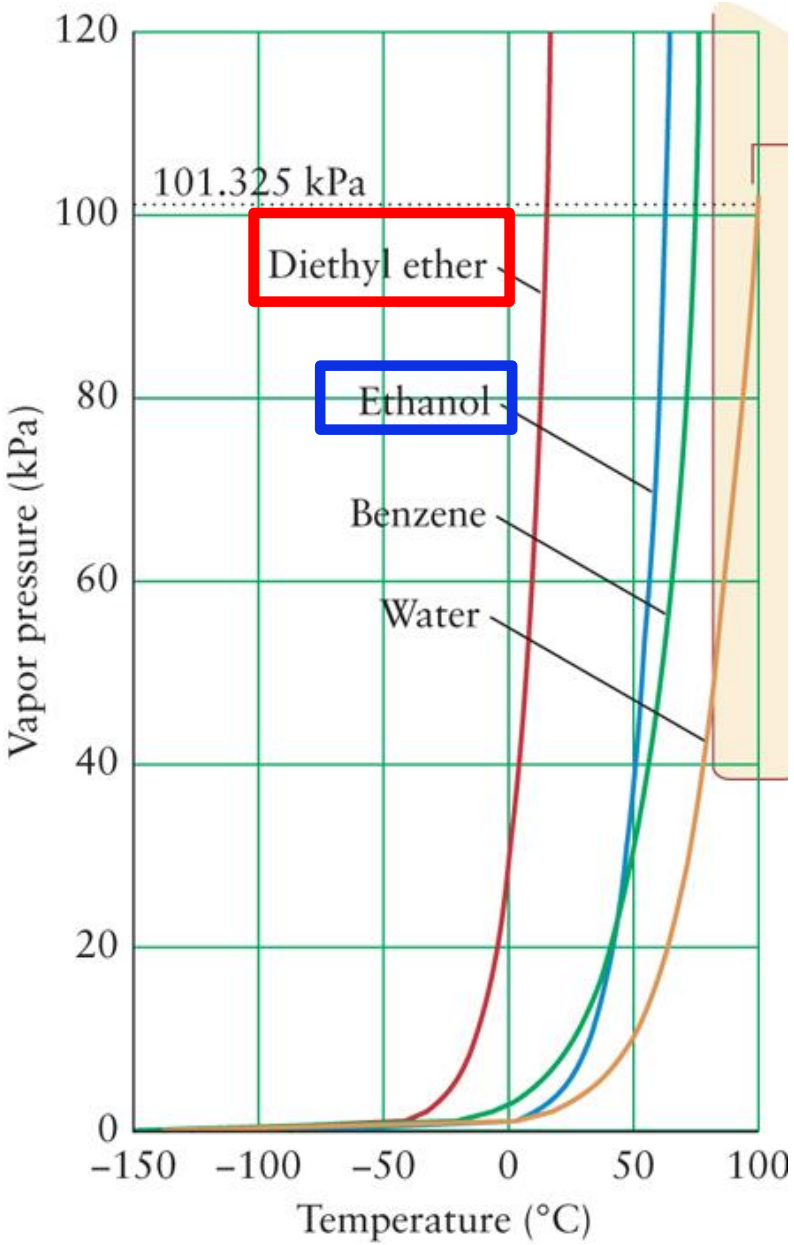
London interactions
verses **Hydrogen bonding**



2 Ethanol

5.83 kPa

@20℃



Clausius – Clapeyron Equation

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

Vapor pressure of liquids at two T

Vapor pressure increases with increasing temperature because:

- $T_2 > T_1$ is positive
- $\ln (P_2/P_1)$ is positive too because enthalpy of vaporization is positive.

$\Delta H_{vap}°$, is a measure of the intermolecular interaction strength (ion-dipole, dipole-dipole, hydrogen boding, London forces).

Example 1: Tetrachloromethane, CCl_4, which is now known to be carcinogenic, was once used as a dry-cleaning solvent. The enthalpy of vaporization of CCl_4 is 33.05 kJ·mol^{-1} and its vapor pressure at 57.8°C is 405 Torr. What is the vapor pressure of terrachloromethane at 25.0°C?

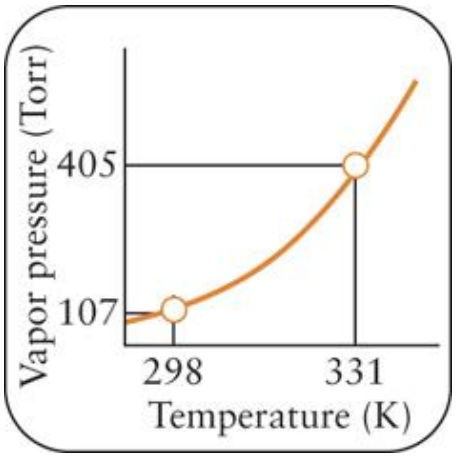
$$\ln \frac{P_2}{P_1} = \frac{\Delta H°_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$\Delta H°_{vap}$ = 33.05 kJ·mol^{-1} corresponds to 3.305 × 10^4 J·mol^{-1}
T_2 = 25.0 + 273.15 K = 298.2 K
T_1 = 57.8 + 273.15 K = 331.0 K
R = 8.3145 J·K^{-1}·mol^{-1}

$$\ln \frac{P_2}{P_1} = \frac{3.305 \times 10^4\ \text{J·mol}^{-1}}{8.3145\ \text{J·K}^{-1}\text{·mol}^{-1}}\left(\frac{1}{331.0\ \text{K}} - \frac{1}{298.2\ \text{K}}\right)$$

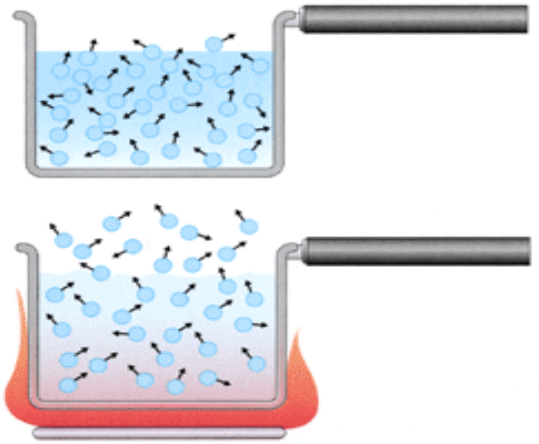
$$\ln \frac{P_2}{P_1} = -1.33, \qquad P_1 = 405\ \text{Torr}$$

$$P_2 = 405\ \text{Torr} \times e^{-1.33} = 107\ \text{Torr}$$



Boiling

Boiling point: the temperature at which the vapor pressure of a liquid is equal to the atmospheric pressure.



The ***normal boiling point***, T_b, is the temperature it boils when the atmospheric pressure is 1 atm.

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

Example 2: The vapor pressure of ethanol at 34.9°C is 13.3 kPa. Use the data in Table 7.3 to estimate the normal boiling point of ethanol.

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

$\Delta H°_{vap} = 43.5\ kJ \cdot mol^{-1}$ or $4.35 \times 10^4\ J \cdot mol^{-1}$
$T_2 = 34.9 + 273.15\ K = 308.0\ K$
$P_2 = 13.3\ kPa$
$P_1 = 101.325\ kPa$ (this corresponds to 1 atm or T_b)
$R = 8.3145\ J \cdot K^{-1} \cdot mol^{-1}$

$$\ln \frac{13.3\ kPa}{101.325\ kPa} = \frac{4.35 \times 10^4\ J \cdot mol^{-1}}{8.3145\ J \cdot K^{-1} \cdot mol^{-1}}\left(\frac{1}{T_1} - \frac{1}{308.0\ K}\right)$$

$$\frac{1}{T_1} = \ln \frac{13.3\ kPa}{101.325\ kPa} \times \frac{8.3145\ J \cdot K^{-1} \cdot mol^{-1}}{4.35 \times 10^4\ J \cdot mol^{-1}} + \frac{1}{308.0\ K}$$

= 350. K or 77°C (Vapor is not a prefect ideal gas.)

Freezing & Melting

Liquids solidify (freeze) when molecules do not have enough energy to wriggle past their neighbors.

The normal freezing point, T_f, is the temperature a liquid freezes at 1 atm.

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

Freezing & Melting

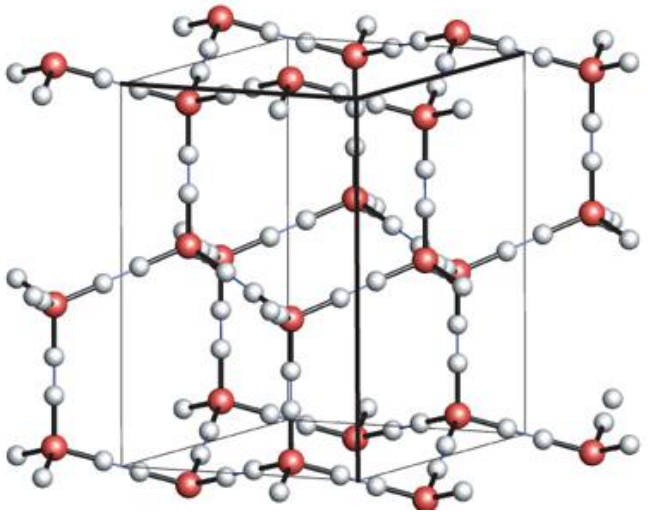
Most substances are more dense in the solid phase than liquid, *water being an exception*.

Water is highly unusual, at 0.0°C, $\text{density}_{\text{liquid}} > \text{density}_{\text{solid}}$

Ice floats on water.

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

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

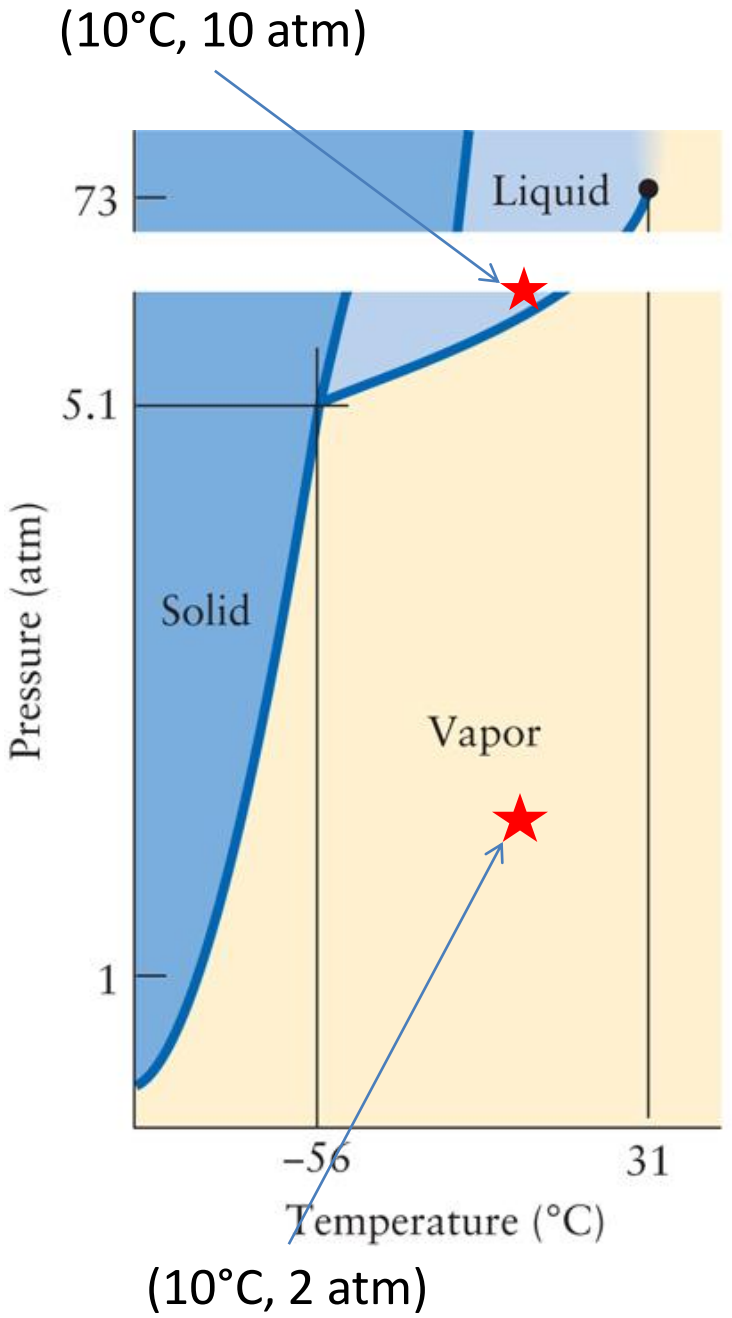


Phase Diagrams

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

The region marked "**solid**" is the solid phase of ice. Other regions indicate marked "**liquid**" and "**vapor**".

This shows that carbon dioxide at 10°C and 2 atm it will be a gas. At 10 atm and 10°C, CO_2 will condense to a liquid.

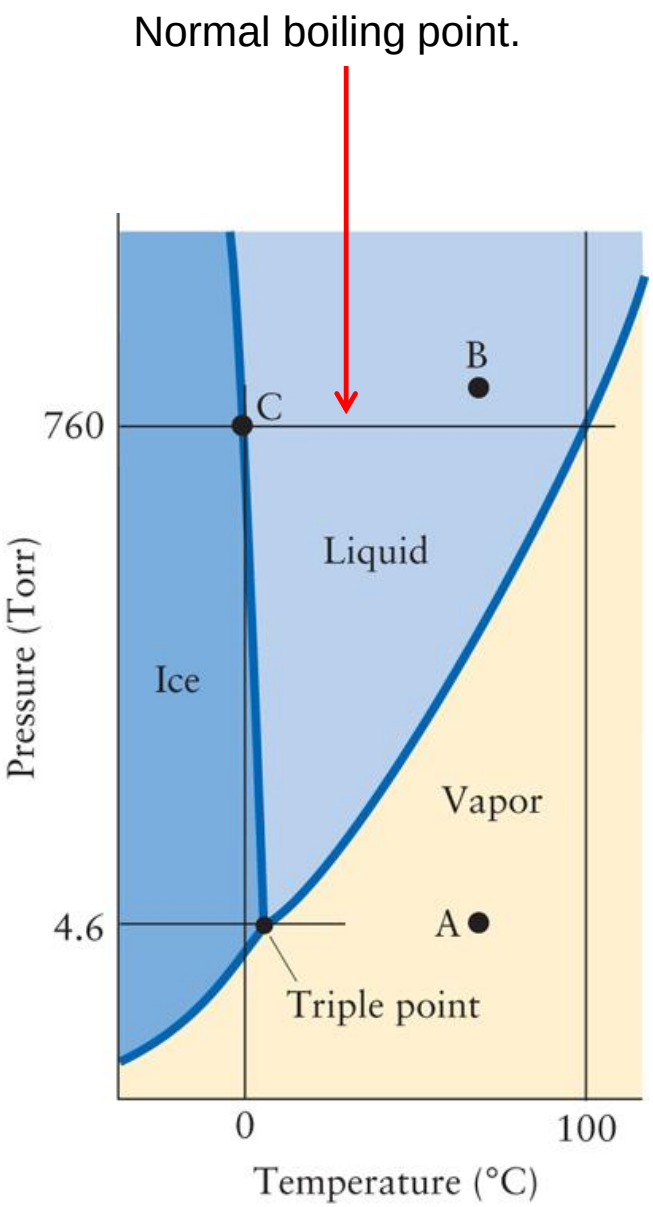


Phase Diagrams

Point “C” is the <u>normal freezing point</u> (0.0°C, 760 Torr).

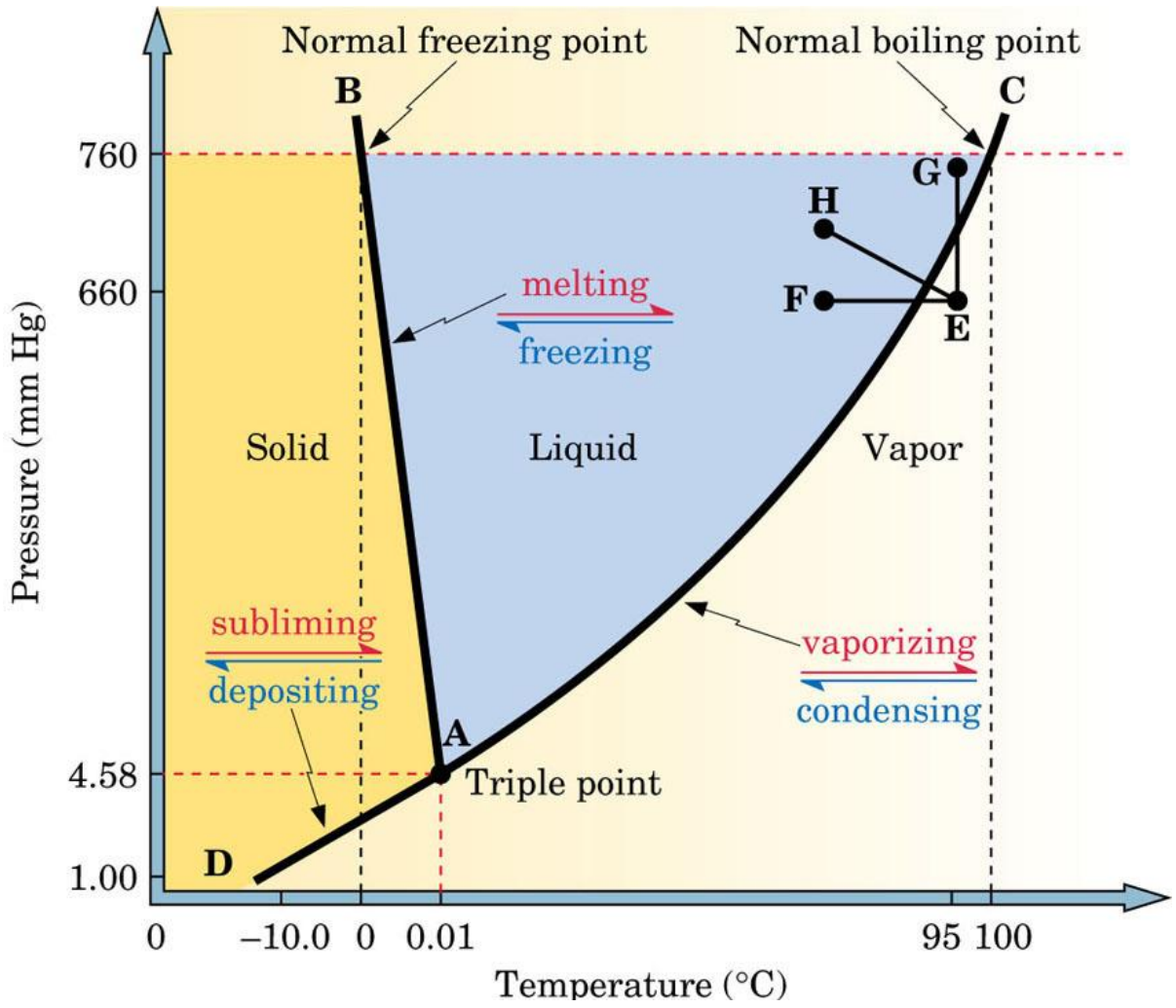
A Triple point is the temperature and pressure where water exists as a **solid**, **liquid**, **vapor**.

The **slope** of the solid-liquid boundary is the ***density*** and for liquid water it is more dense than its solid. Therefore, **notice** that as we increase the pressure of ice, it will eventually be converted to liquid (ice-skating).



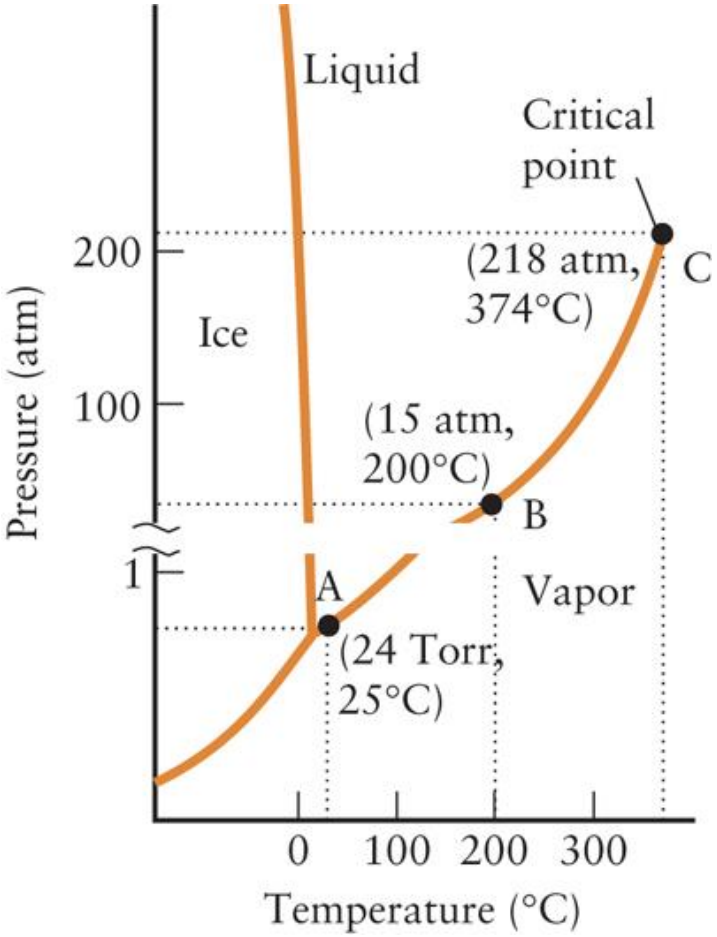
Phase Diagrams: water

Phase Diagrams



Phase Diagrams: water

Critical Properties



There is an <u>end in the liquid-vapor phase boundary</u> called the critical point.

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

Critical point: vapor **density** = liquid **density**

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

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

Solutions

Saturated: solvent contains or holds all the solute it can (at a given T).

maximum solute that solvent can hold (Equilibrium).

Unsaturated: solvent can hold more solute (at a given T).

Is not the maximum solute that solvent can hold.

Supersaturated: solvent holds more solute that it can normally hold (at a given T).

↓

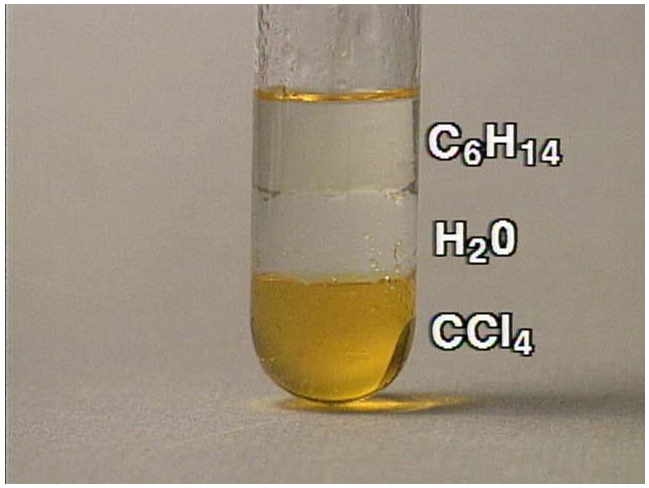
(more than an equilibrium condition)

Solvent and Solute

Polar dissolves polar

Nonpolar dissolves nonpolar

⇨ like dissolves like.



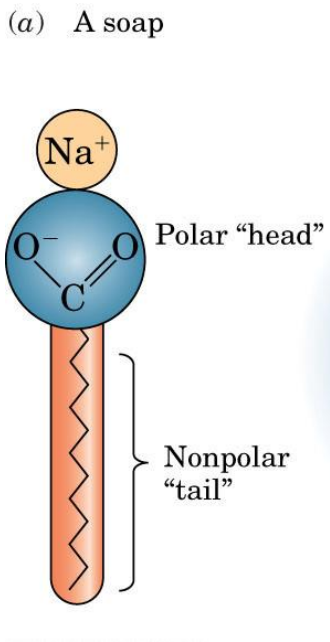
Soaps

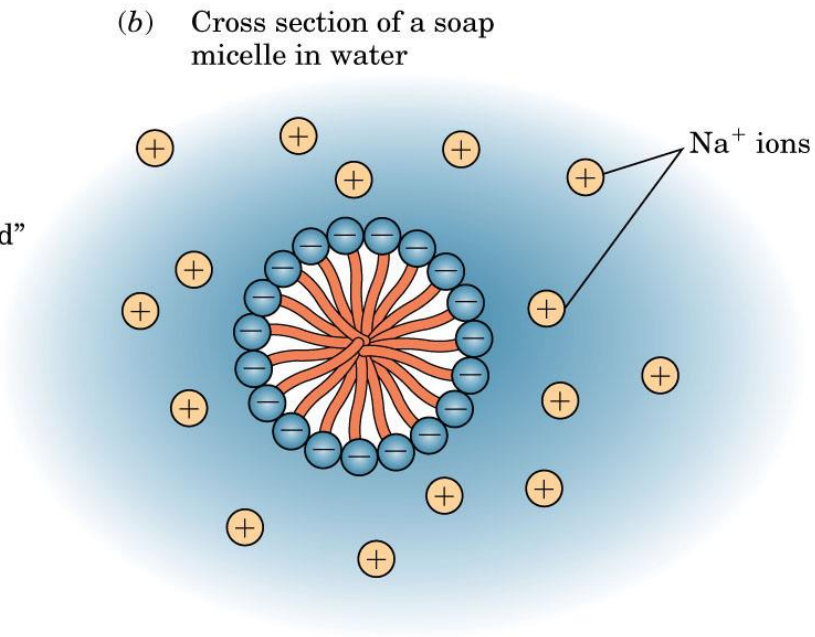
Hydrophobic part: nonpolar

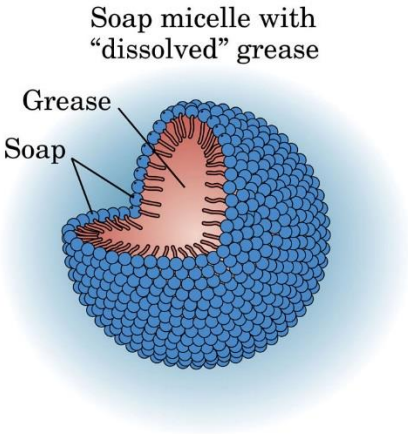
Hydrophilic part: polar (remains in contact with environment-water)

$$3\,RCO^{-}Na^{+}$$

Sodium soaps



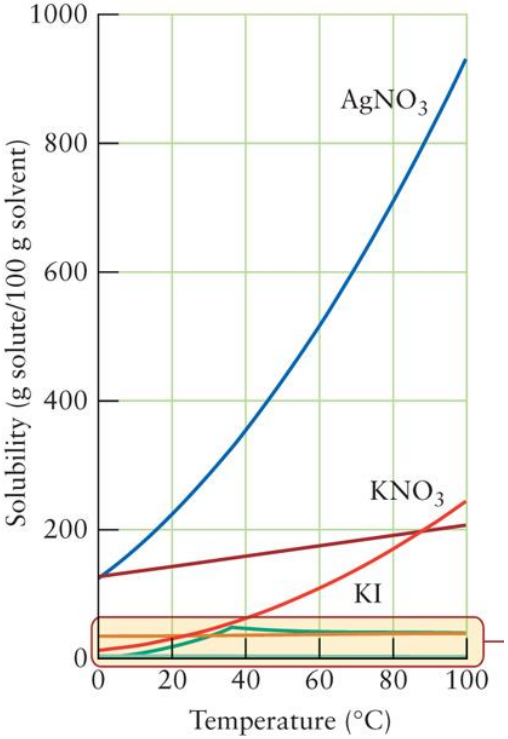




Temperature and Solutions

Solubility: the maximum solute that will dissolve in a given amount of a solvent (at a given T).

T ↑ ⟹ Solubility ↑



T ↓ ⟹ Crystal is formed.

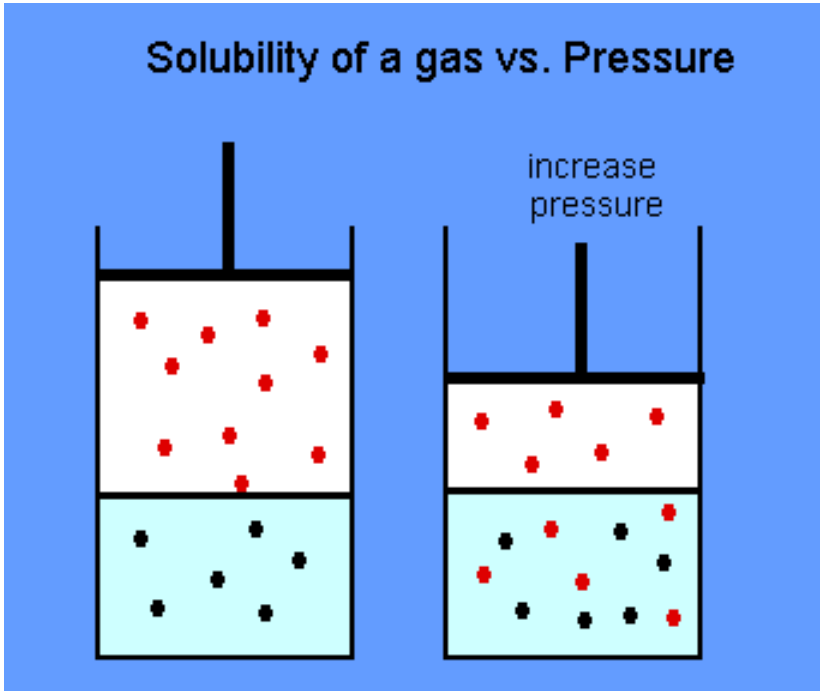
Temperature and Solutions

Gas in Liquid: T ↑ ⇨ Solubility ↓

Global Warming

Pressure and Solutions

Henry's law P ↑ ⟹ Solubility ↑ (gas in liquid)



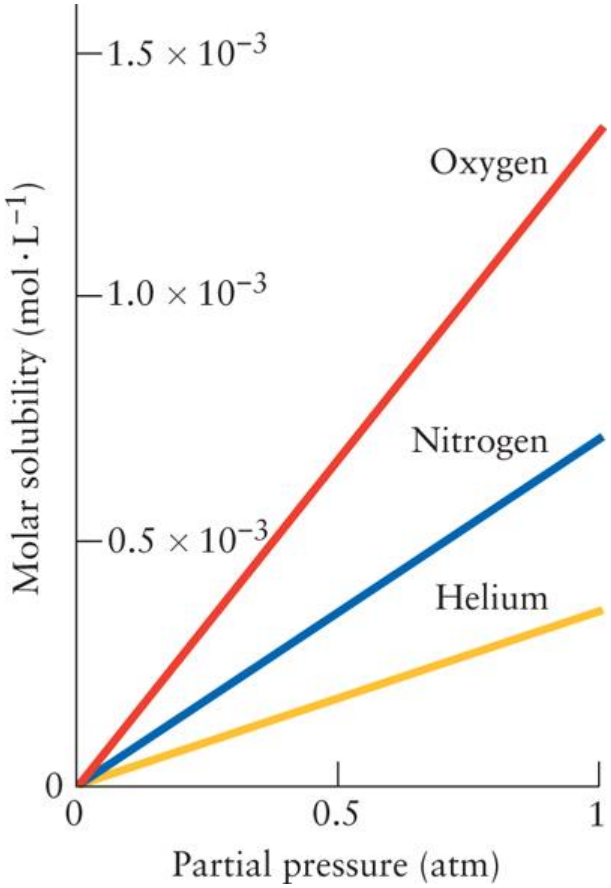
Pressure and Solutions

The **solubility** of a **gas** ***is directly proportional*** to its **partial pressure, P**.

$$s = k_H P$$

k_H is called Henry's constant.

(depends on gas, the solvent, and T)



Example 3: Verify that the concentration of oxygen in lake water is normally adequate to sustain aquatic life, which requires a concentration of at least 0.13 mmol·L^{-1}. The partial pressure of oxygen is 0.21 atm at sea level.

From $s = k_H P$

$k_H = 1.3 \times 10^{-3}$ mol·L^{-1}·atm^{-1}

$s = (1.3 \times 10^{-3}$ mol·L^{-1}·$atm^{-1}) \times 0.21$ atm

$= 2.7 \times 10^{-4}$ mol·L^{-1} which is much greater than 0.13 mmol·L^{-1}

Enthalpy of Solution

Measuring heat released or absorbed when a substance dissolves is called molar enthalpy of solution, ΔH_{sol}.

	Anion							
Cation	fluoride	chloride	bromide	iodide	hydroxide	carbonate	sulfate	nitrate
lithium	+4.9	−37.0	−48.8	−63.3	−23.6	−18.2	−2.7	−29.8
sodium	+1.9	+3.9	−0.6	−7.5	−44.5	−26.7	+20.4	−2.4
potassium	−17.7	+17.2	+19.9	+20.3	−57.1	−30.9	+34.9	+23.8
ammonium	−1.2	+14.8	+16.0	+13.7	—	—	+25.7	+6.6
silver	−22.5	+65.5	+84.4	+112.2	—	+41.8	+22.6	+17.8
magnesium	−12.6	−160.0	−185.6	−213.2	+2.3	−25.3	−90.9	−91.2
calcium	+11.5	−81.3	−103.1	−119.7	−16.7	−13.1	−19.2	−18.0
aluminum	−27	−329	−368	−385	—	—	—	−350

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

Enthalpy of Solution

The first step sublimes solids ions to gas ions. Highly endothermic, this is the lattice enthalpy, ΔH_L, for NaCl;

$$NaCl(s) + 787\ kJ{\cdot}mol^{-1} \rightarrow Na^+(g) + Cl^-(g)$$

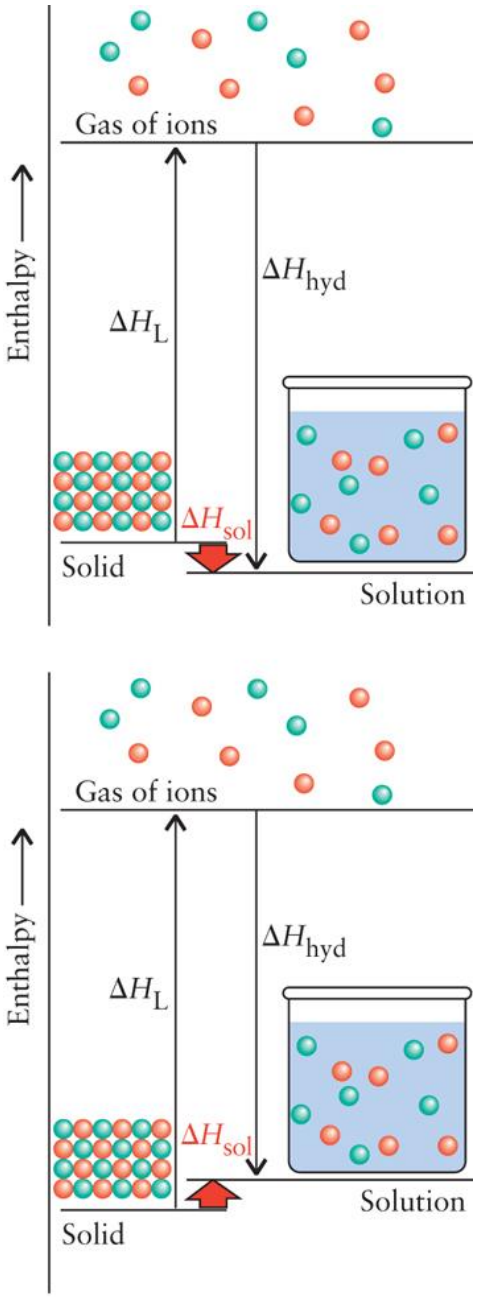
The second step, gaseous ions plunge into water forming the final solution. This is the enthalpy of hydration, ΔH_{hyd}, and for NaCl;

$$Na^+(g) + Cl^-(g) \rightarrow Na^+(aq) + Cl^-(aq) + 784\ kJ{\cdot}mol^{-1}$$

Combing these steps : $\mathbf{\Delta H_{sol}} = \Delta H_L + \Delta H_{hyd}$

$\mathbf{\Delta H_{sol}} = \{787 + (-784)\}\ kJ{\cdot}mol^{-1} = +3\ kJ{\cdot}mol^{-1}$ (endothermic)

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



Enthalpy of Solution

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

High charge and **small ionic radius** contribute to ***high*** lattice enthalpy (ΔH_L).

However, often *these can be the same properties* that related to ***low*** enthalpy of hydration (ΔH_{hyd}).

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

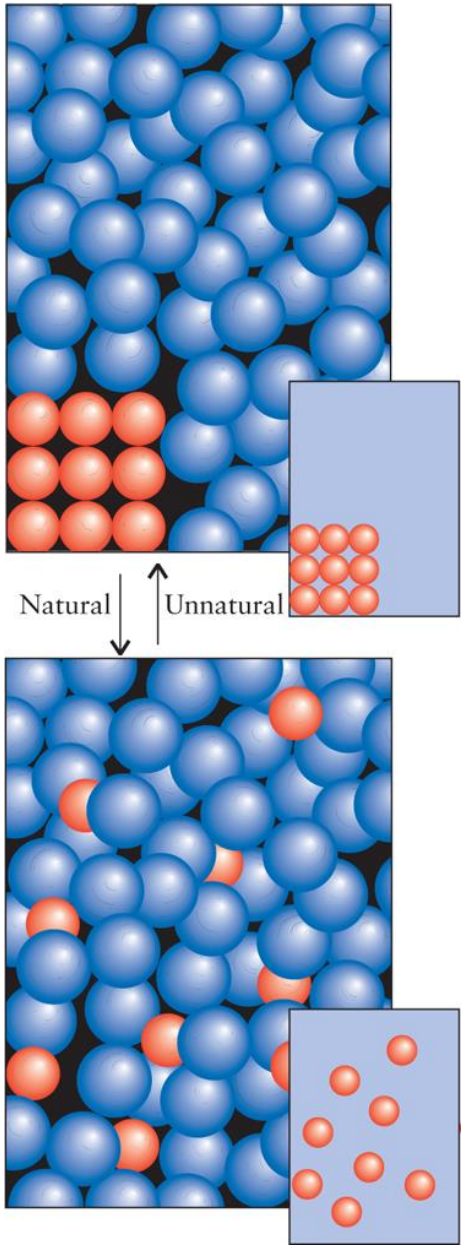
Nitrates, **NO_3^-**, have a *big, single charged anions*, so have a **small** ΔH_L. But these same features mean that the ΔH_{hyd} is **very large** resulting in a **ΔH_{sol} (↑)**. This is why nitrates are rarely found in mineral deposits because they are soluble.

Carbonate ions, **CO_3^{2-}**, are about the same size as nitrate ions, but they are doubly charged. They have a low **ΔH_{sol} (↓)** because they have **very high** ΔH_L (2-charge and size) and **low** ΔH_{hyd}; so found in limestone.

The Gibbs Free Energy of Solution

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

A <u>negative enthalpy</u>, $-\Delta H_{sol}$, is an **energy releasing** process.



An increase in ΔS

Dissolving a solid increases the disorder of a system, so we expect ΔS to increase or be positive.

The Gibbs Free Energy of Solution

If ΔH is negative, dissolving would be a spontaneous change (at constant temperature and pressure). Compound is soluble.

$$\Delta G = \Delta H - T\Delta S.$$

In dissolving: ΔS_{tot} = Positive

If ΔH is positive, dissolving would be a spontaneous change if $T\Delta S$ is positive and larger than ΔH. Higher temperature makes a compound more soluble.

At equilibrium: $\Delta S = 0$, so $\Delta G = 0$

Colligative Properties

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 the:

1. lowering of the vapor pressure,
2. raising boiling points,
3. lowering of freezing points, and
4. osmosis.

Extensive properties depend on the quantity of matter (*n* atoms), Volume & Mass whereas intensive properties are independent of the quantity of matter, Density & Temperature. Colligative is a new third category.

Molality

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

$$\textbf{molality} = \frac{\text{amount of solute (mol)}}{\text{mass of solvent (kg)}}$$

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

Units of *molality* $mol \cdot kg^{-1}$ and denoted as "**m**" for example, a 1.0 m $NiSO_4(aq)$ and read as "**molal**" is exactly 1 mol $NiSO_4$ dissolved in 1 kg of water.

Molality

Example 4: What is the molality of NaCl in a solution prepared by dissolving 10.5 g of sodium chloride in 250. g of water?

$$\text{Molality} = \frac{\text{moles solute}}{\text{Kg solvent}}$$

$$10.5\text{g NaCl} \times \frac{1\text{ mol NaCl}}{58.5\text{ g NaCl}} = 0.179\text{ mol NaCl}$$

$$250.\text{g } H_2O \times \frac{1\text{ kg } H_2O}{1000\text{ g } H_2O} = 0.250\text{ kg } H_2O$$

$$m = \frac{0.179\text{ mol NaCl}}{0.250\text{ kg } H_2O} = 0.716\text{ m}$$

Useful Equations

Mole fraction: $\chi_{solute} = \frac{n_{solute}}{n_{solute} + n_{solvent}}$ or $\chi_{solvent} = \frac{n_{solvent}}{n_{solute} + n_{solvent}}$

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

Calculating the mass of solvent from mole fraction:

$m_{solvent}\,(g) = n_{solvent}\,(mol)\; M_{solvent}\,(g \cdot mol^{-1}) = \{(1 - \chi_{solute})(mol)\}\; M_{solvent}\,(g \cdot mol^{-1})$

Calculating the molality, given the molarity:

$m_{solute}(g) = n_{solute}\,(mol)\; M_{solute}\,(g \cdot mol^{-1}) = molarity(mol \cdot L^{-1}) \times 1L \times M_{solute}(g \cdot mol^{-1})$

$m_{solvent}\,(g) = m_{solution}\,(g) - m_{solute}\,(g)$

Example 5: What is the molality of benzene, C_6H_6, dissolved in toluene, $C_6H_5CH_3$, in a solution for which the mole fraction of benzene is 0.150 ?

$$\text{molality} = \frac{n_{solute}\ (\text{mol})}{m_{solvent}\ (\text{kg})}$$

First we find the mass, kg, of toluene

benzene, C_6H_6 is the solute, and toluene is the solvent.

78.11 $g \cdot mol^{-1}$ C_6H_6
92.13 $g \cdot mol^{-1}$ $C_6H_5CH_3$

Calculating the mass of solvent from mole fraction:

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

$\{(1 - 0.150)\ mol\} \times 92.13\ g \cdot mol^{-1} = 78.3$ g toluene $= 0.0783$ kg toluene

$$m = \frac{n_{solute}}{kg_{solvent}} = \frac{0.150\ \text{mol benzene}}{0.0783\ \text{kg toluene}} = 1.92\ mol \cdot kg^{-1}$$

Example 6: 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 $g.mL^{-1}$.

$$\text{molality} = \frac{n_{solute}\ (mol)}{m_{solvent}\ (kg)}$$

342.3 $g \cdot mol^{-1}$ $C_{12}H_{22}O_{11}$

Calculating the molality, given the molarity:

$m_{solute}\ (g) = n_{solute}\ (mol)\ M_{solute}\ (g \cdot mol^{-1})$ = molarity $(mol \cdot L^{-1}) \times 1L \times M_{solute}\ (g \cdot mol^{-1})$

$m_{solvent}\ (g) = m_{solution}\ (g) - m_{solute}\ (g)$

Example 6: 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 $g.mL^{-1}$.

Mass of solvent must be calculated per liter since we're working with molarity: 1.14 $g.mL^{-1}$ × 1000 mL = 1140 g of solution (we use this in the 2nd equation to find the mass of solvent).

Next, mass of solute = molarity × (1L) × M_{solute},

(1.06 $mol \cdot L^{-1}$) × 1L × 342.3 $g \cdot mol^{-1}$ = 363 g solute (sucrose)

$m_{solvent}$ (g) = $m_{solution}$ (g) – m_{solute} (g),

1140 g solution - 363 g solute = 780 g or 0.78 kg

$$n_{sucrose} = 363g\ C_{12}H_{22}O_{11} \times \frac{1\ mol\ C_{12}H_{22}O_{11}}{342.3\ g\ C_{12}H_{22}O_{11}} = 1.06\ mol\ C_{12}H_{22}O_{11}$$

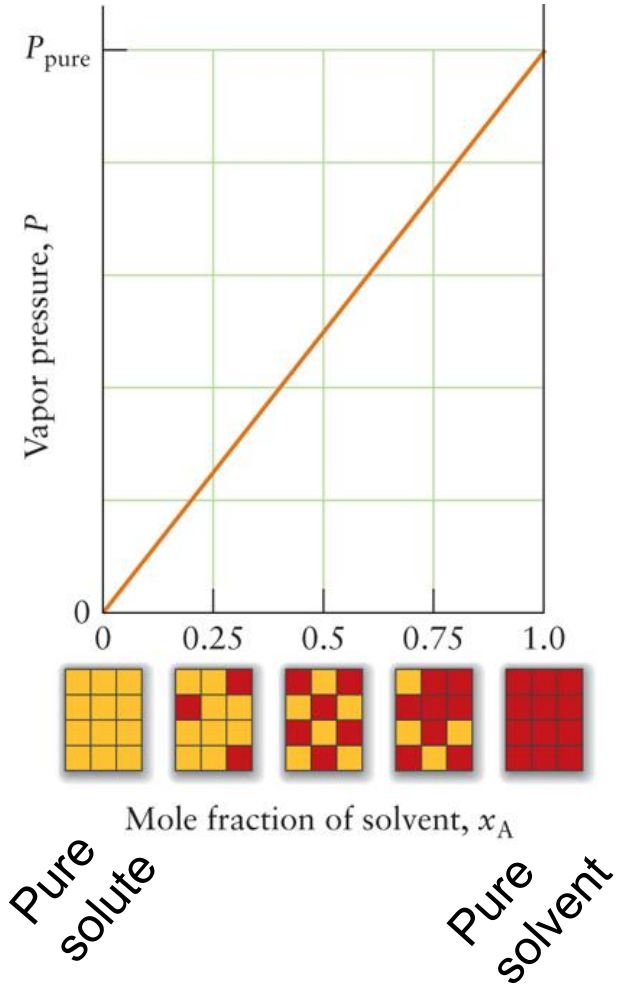
$$m = \frac{1.06\ mol}{0.78\ kg} = 1.4\ mol \cdot kg^{-1}$$

Vapor-Pressure Lowering

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

$$P = \chi_{solvent} P_{pure}$$

P is the vapor pressure of the solvent, $X_{solvent}$ is the mole fraction of the solvent, and P_{pure} is the vapor pressure of the pure solvent.



Example 7: Calculate the vapor 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.

Using $P = \chi_{solvent} P_{pure}$ to find P we need to find $\chi_{solvent}$

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

P_{pure} is 17.54 Torr at 20.°C(table 10.3)

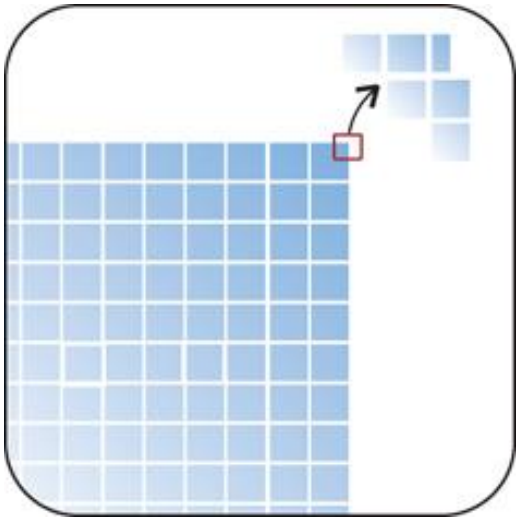
$$n_{surose} = 10.00\text{g } C_{12}H_{22}O_{11} \times \frac{1 \text{ mol } C_{12}H_{22}O_{11}}{342.3 \text{ g } C_{12}H_{22}O_{11}} = 0.02921 \text{ mol } C_{12}H_{22}O_{11}$$

$$n_{water} = 100.0\text{g } H_2O \times \frac{1 \text{ mol } H_2O}{18.015 \text{ g } H_2O} = 5.551 \text{ mol } H_2O$$

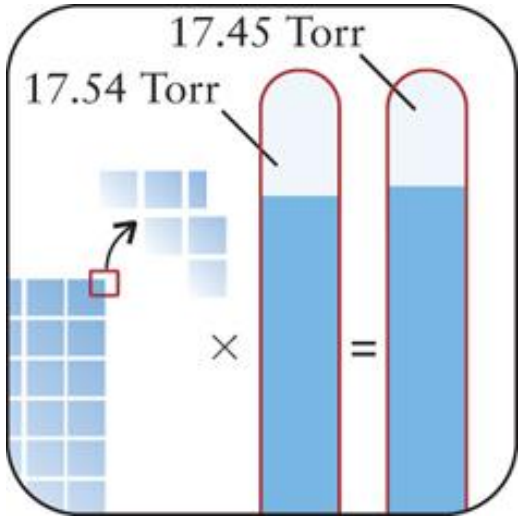
Example 7: Calculate the vapor pressure of water at 20.°C in a solution prepared by dissolving 10.00 g of the nonelectrolyte sucrose, $C_{12}H_{22}O_{11}$, in 100.0 g of water.

$$\chi_{solvent} = \frac{5.551 \text{ mol } H_2O}{0.02921 \text{ mol } C_{12}H_{22}O_{11} + 5.551 \text{ mol } H_2O} = 0.995$$

$P = \chi_{solvent} P_{pure}$, (0.995) × 17.54 Torr = 17.45 Torr (not much of a change)



½ 1%



Raoult's Law

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

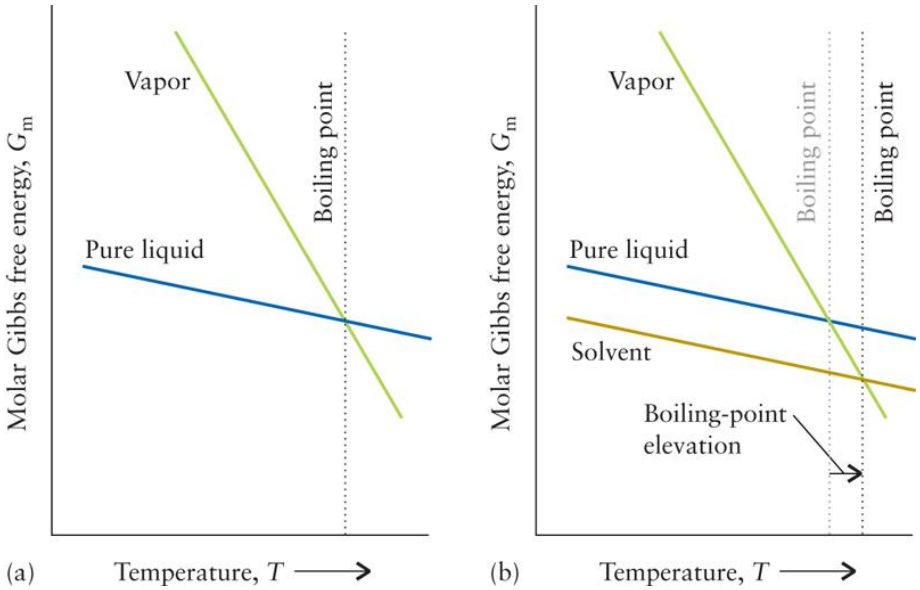
Real solutions are approximately ***ideal*** at concentrations below about **0.1 M for nonelectrolyte** (sugar) solutions and **0.01 M for electrolyte** solutions (ionic).

Raoult's law is another example of a limiting law.

Boiling-Point Elevation and Freezing-Point Depression

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

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



The increased 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.

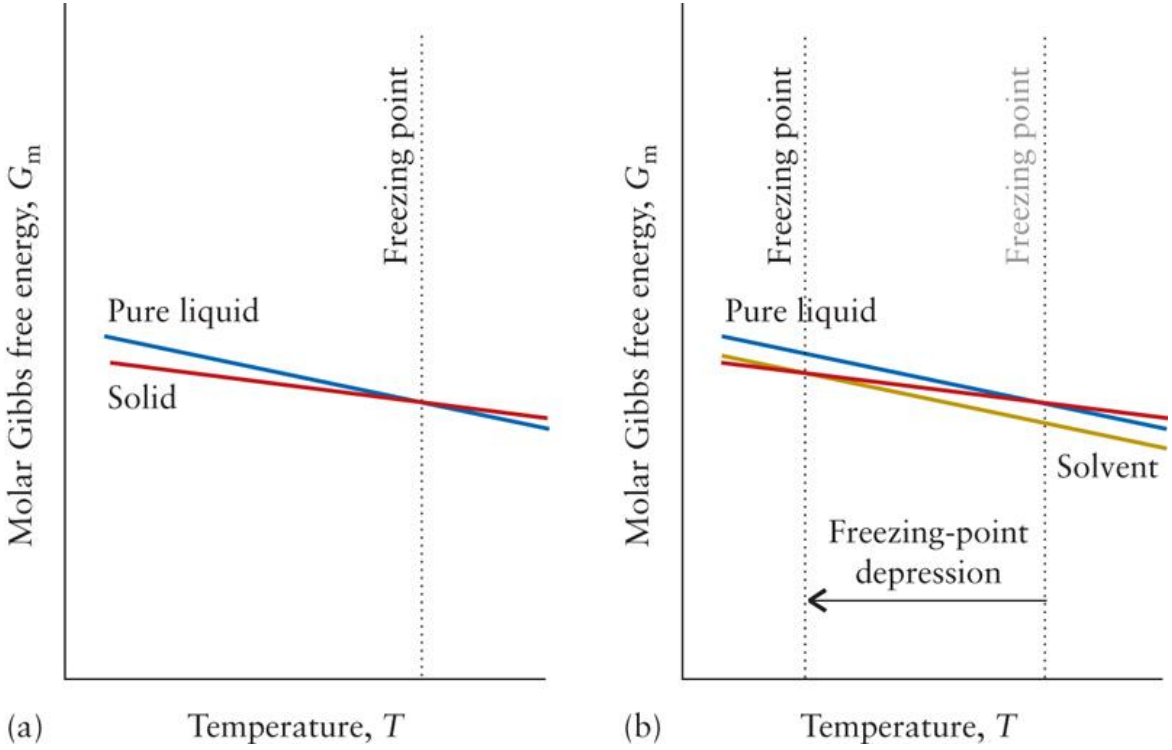
Boiling-Point Elevation and Freezing-Point Depression

Freezing-point depression is more significance. 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 waters freezing point melting it.

Melting point are also a method for determining the **purity of a solid.**



Boiling-Point Elevation and Freezing-Point Depression

Freezing-point depression = k_f × molality, temp. **decreases**.

Boiling-point elevation = k_b × molality, temp. **increases**.

Solvent	Freezing point (°C)	k_f (K·kg·mol^{-1})	Boiling point (°C)	k_b (K·kg·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

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

Freezing-point depression = (1.86 K·kg·mol^{-1}) × (0.1 mol·kg^{-1}) = 0.2 K, so water would freeze at -0.2°C.

Boiling-Point Elevation and Freezing-Point Depression

In an *electrolyte solution*, each formula unit contributes two or more ions. Sodium chloride, gives Na^+ and Cl^- ions, and both ions contribute to the depression of the freezing point.

Solve for freezing point = ik_f × molality

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

In very dilute solution, less than 0.001 M, where all ions are independent, i = 2 for MX salts such as NaCl, and for MX_2 salts such as $CaCl_2$, i = 3.

Example 8: 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.

- First, we recognize to find molar mass of the solute, M_{solute}, that M_{solute} = $g \cdot mol^{-1}$
- Second, we can use that information to find the formula M_{solute}/atomic mass
- In the first step, using freezing point = ik_f × molality , we solve for molality. Since m = $mol \cdot kg^{-1}$ we can find mol, which is part of the first step.

  k_f (CCl_4) = 29.8 $K \cdot kg \cdot mol^{-1}$
  i = 1 for a nonelectrolyte
  The change in temperature 0.28°C = 0.28K
  100. g = 0.100 kg

Example 8: 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.

Solve for freezing point = $ik_f \times$ molality

$$\text{Molality} = \frac{\text{freezing point}}{ik_f} = \frac{0.28\text{K}}{(1) \times (29.8\ \text{K}\cdot\text{kg}\cdot\text{mol}^{-1})} = 0.0094\ \text{m}$$

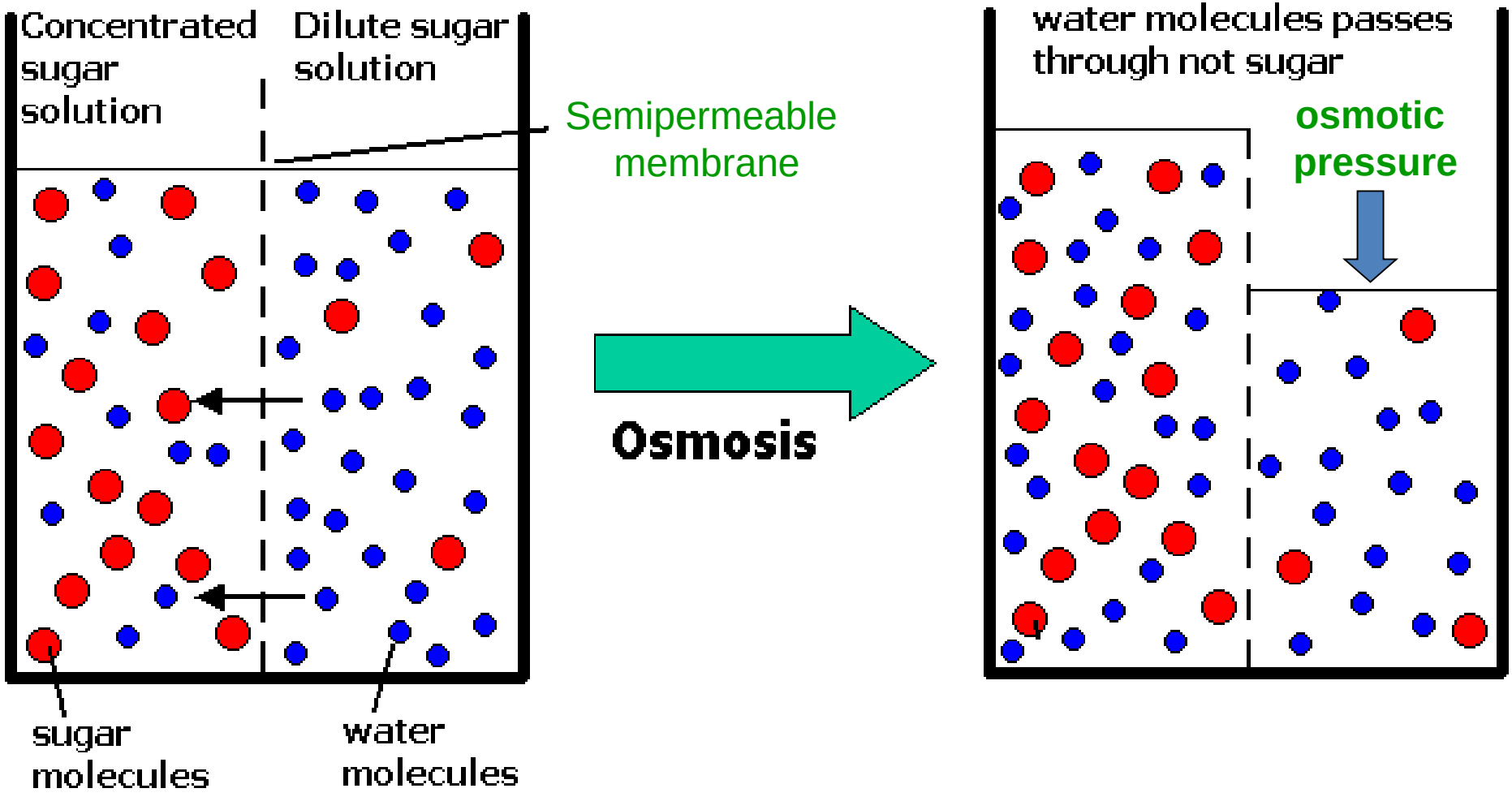
$$\text{Molality} = \frac{\text{moles solute}}{\text{Kg solvent}}$$

$$0.0094\ \text{m} = \frac{\text{mole solute}}{0.100\text{kg solvent}} \Rightarrow \text{mole solute} = 0.00094\ \text{mole sulfur}$$

$$\text{First part, g}\cdot\text{mol}^{-1} = \frac{0.24\ \text{g}}{0.00094\ \text{mol}} = 2.6 \times 10^2\ \text{g}\cdot\text{mol}^{-1}$$

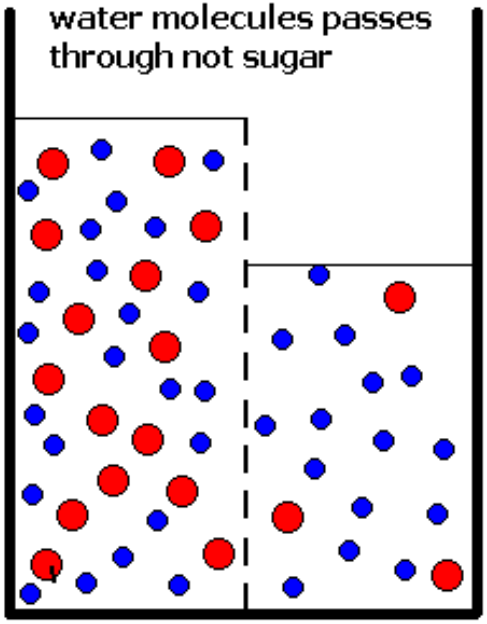
$$\text{Second part, } M_{solute}/\text{atomic mass} = \frac{2.6 \times 10^2\ \text{g}\cdot\text{mol}^{-1}}{32.1\ \text{g}\cdot\text{mol}^{-1}} = 8.1, \text{ so } S_8$$

Osmosis



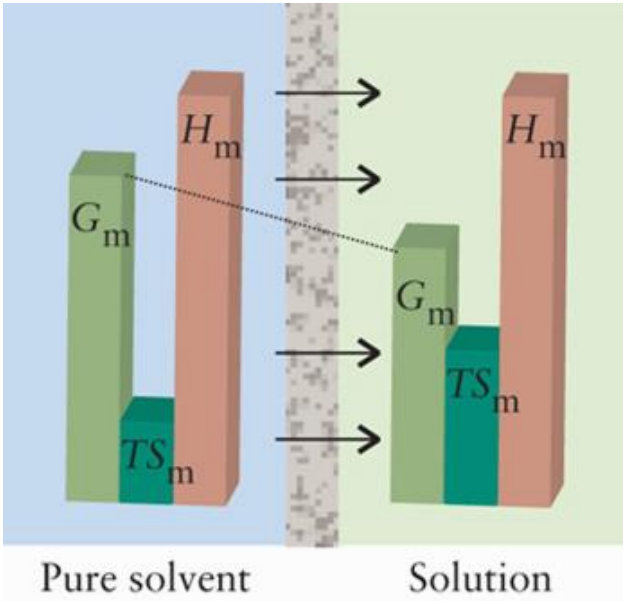
Higher concentration → Higher osmotic pressure

Osmosis

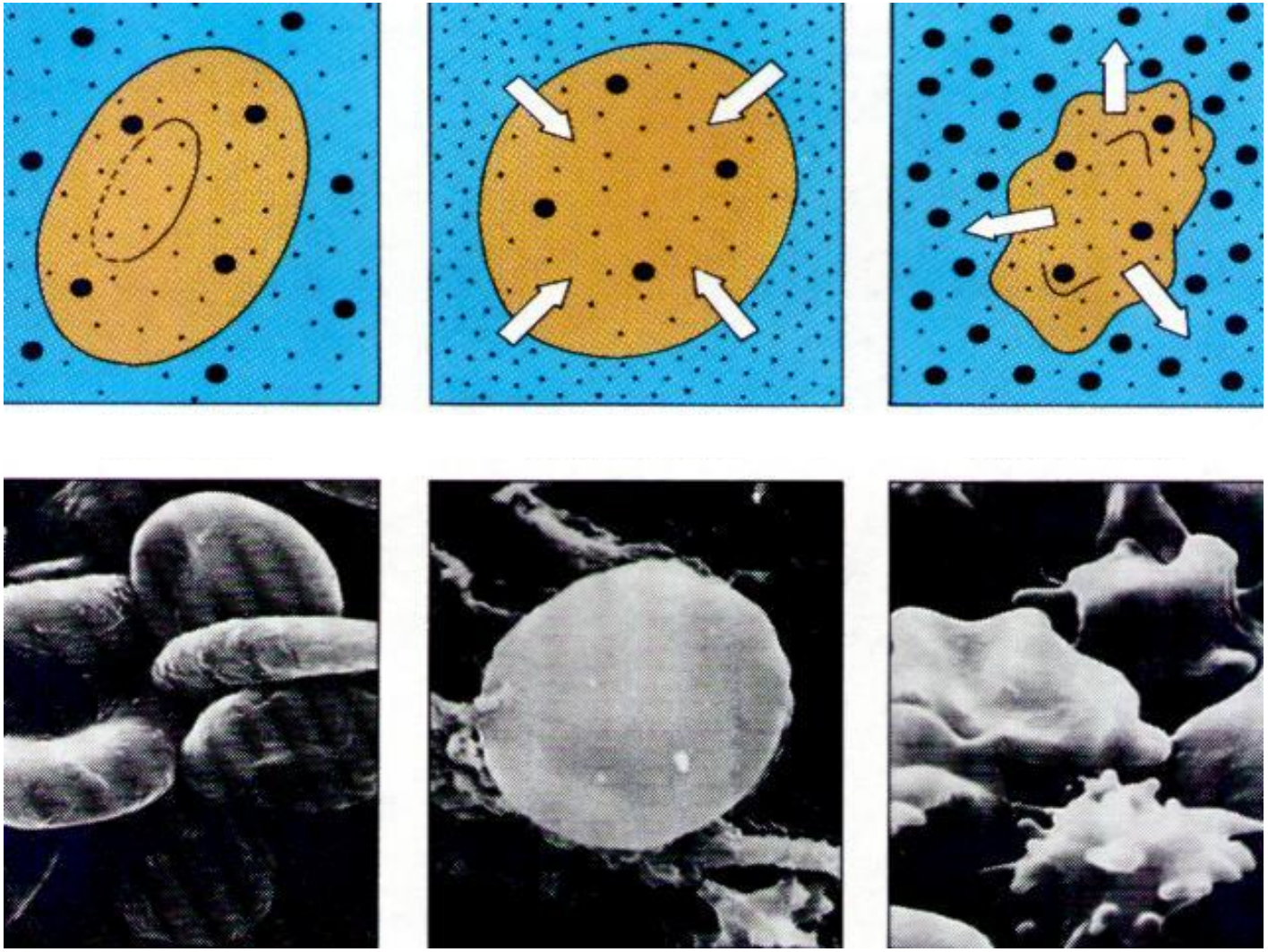


Water flows from
low concentration
to
high concentration.

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



Isotonic solution **Hypotonic solution** **Hypertonic solution**



Hemolysis Crenation

Osmosis

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

$\Pi = iRTc$ (also $\Pi = iRTM$ where M is molarity)

c is molarity,
R is the gas constant,
T is temperature.

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

Example 9: What is the osmotic pressure of a 0.120 M NaCl solution at 298 K?

The van't Hoff i factor is 2 for a electrolyte substance like NaCl.

$\Pi = iRTc$,

$(2) \times (0.08206\ \text{atm}\cdot\text{L}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) \times (298\ \text{K}) \times (0.120\ \text{mol}\cdot\text{L}^{-1}) = 5.86\ \text{atm}$

Practice 1: The normal boiling point of iodomethane, CH3I, is 42.43ºC, and its vapor pressure at 0.00ºC is 140. torr. Calculate (a) the standard enthalpy of vaporization of iodomethane; (b) the standard entropy of vaporization of iodomethane; © the vapor pressure of iodomethane at 25.0ºC?

Practice 2: Which would be the better solvent, water or benzene, for each of the following substances: (a) KCl; (b) CCl_4; (c) CH_3COOH?

Practice 3: Calculate the molality of KOH in a solution prepared from 3.12g of KOH and 67.0g of water.

Practice 4: The density of 14.8M $NH_3(aq)$ is 0.901 $g.cm^{-3}$. What is the molality of NH_3 in the solution?

Practice 5: A 1.14-g sample of a molecular substance dissolved in 100. g of camphor freezes at 176.9ºC. What is the molar mass of the substance?

Practice 6: What is the osmotic pressure at 20ºC of (a) 0.010M $C_{12}H_{22}O_{11}(aq)$; (b) 1.0M HCl(aq); (c) 0.010M $CaCl_2(aq)$? Assume complete dissociation of the $CaCl_2$.