

➤ **Mole Fraction**

$$X_1 = \frac{n_1}{n_1 + n_2}, \quad X_2 = \frac{n_2}{n_1 + n_2} = 1 - X_1 \quad (\text{for a binary mixture})$$

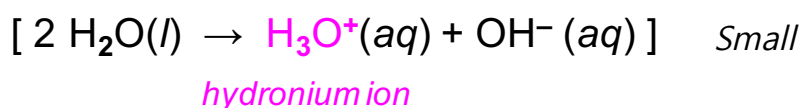
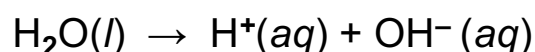
➤ **Molarity & Molality**

$$\text{Molarity (M)} = \frac{\text{moles solute}}{\text{liters solution}} = \text{mol L}^{-1}$$

$$\text{Molality (m)} = \frac{\text{moles solute}}{\text{kilograms solvent}} = \text{mol kg}^{-1}$$

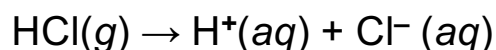
✓ Molality is independent of temperature!

➤ **Ionization of pure water**

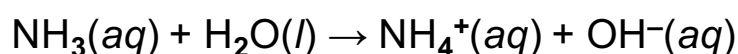
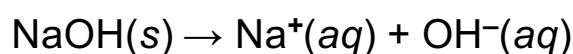


➤ **Arrhenius's definition of Acids and Bases**

Acid ~ produces  $\text{H}^+$  ( $\text{H}_3\text{O}^+$ ) in aqueous solution ( $> [\text{H}^+]_{\text{water}}$ )



Base ~ produces  $\text{OH}^-$  in aqueous solution ( $> [\text{OH}^-]_{\text{water}}$ )



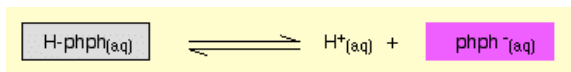
## ➤ Titration

Determination of unknown amount of a sample

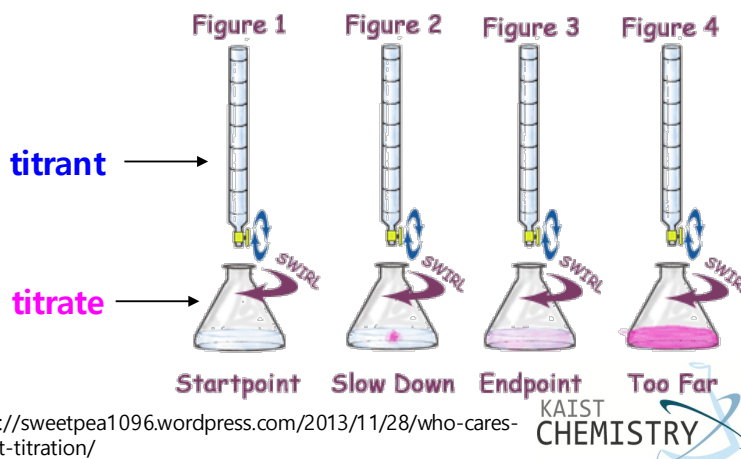
Titrant (in buret, known concentration, volume to be measured)

→ Titrate (in flask, unknown concentration, known volume)

End point, Indicator



### Titration of an Acid with a Base using phenolphthalein indicator



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## 11.4 REACTION STOICHIOMETRY IN SOLUTIONS: OXIDATION-REDUCTION TITRATIONS

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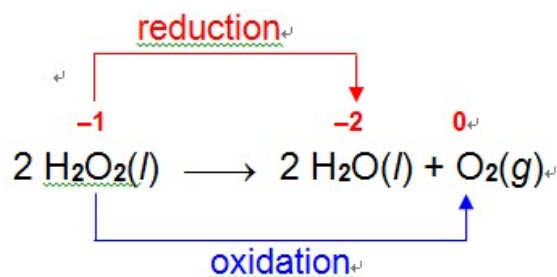
### ➤ Background on Oxidation-Reduction (Redox) Reactions

Oxidation ~ increase in the oxidation number, donate electrons

Reduction ~ decrease in the oxidation number, accept electrons

### ➤ Disproportionation

~ Redox reaction in which a single substance is both oxidized and reduced.



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## 11.5 PHASE EQUILIBRIUM IN SOLUTIONS: NONVOLATILE SOLUTES

The solvent vapor pressure changes with the composition of the solution at a fixed temperature.

### ➤ Raoult's law

~ for Ideal solutions

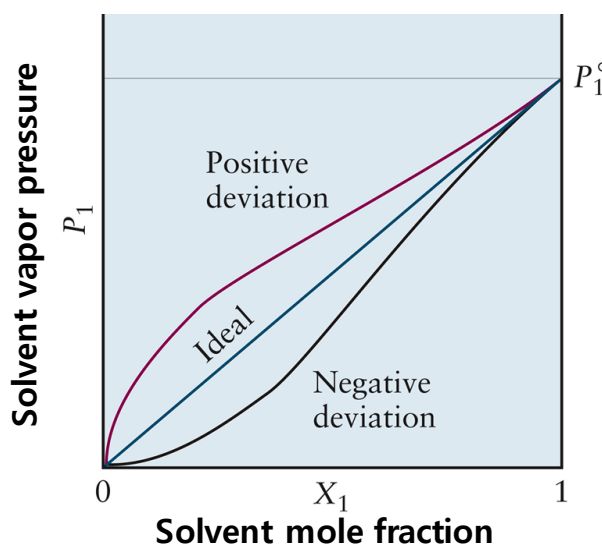
Vapor pressure of **solvent** in solution

$P_1 \propto$  its mole fraction  $X_1$

$$P_1 = X_1 P_1^\circ$$

$P_1^\circ$  : vapor press of pure solvent

Plot of  $P_1$  vs.  $X_1$  ~ a straight line



**Fig. 11.10** Vapor pressure of solvent in ideal and nonideal solutions.

### ◆ Colligative properties

Collective properties depending on the *number* of dissolved particles rather than the *nature* of the particular particles involved

→ Determination of *Molar mass (mass per mole), molality(m)*

Let us consider

Nonvolatile solute, Nonelectrolyte, Binary solution

- ❖ Vapor pressure lowering
- ❖ Boiling-point elevation
- ❖ Freezing-point depression
- ❖ Osmosis

## ➤ Vapor-Pressure Lowering

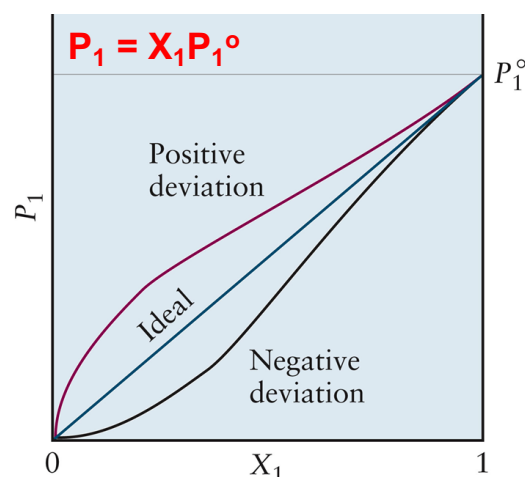
$$P_1 = X_1 P_1^\circ \quad \text{Raoult's law}$$

2 component solution :  $X_1 + X_2 = 1$

$\left\{ \begin{array}{l} 1: \text{solvent} \\ 2: \text{solute} \end{array} \right.$

$$\Delta P_1 = P_1 - P_1^\circ = X_1 P_1^\circ - P_1^\circ = -X_2 P_1^\circ$$

$$\Delta P_1 = -X_2 P_1^\circ$$



$P_1$  (above a dilute solution)  $< P_1^\circ$  (above a pure solvent)

## ❖ Boiling-point elevation

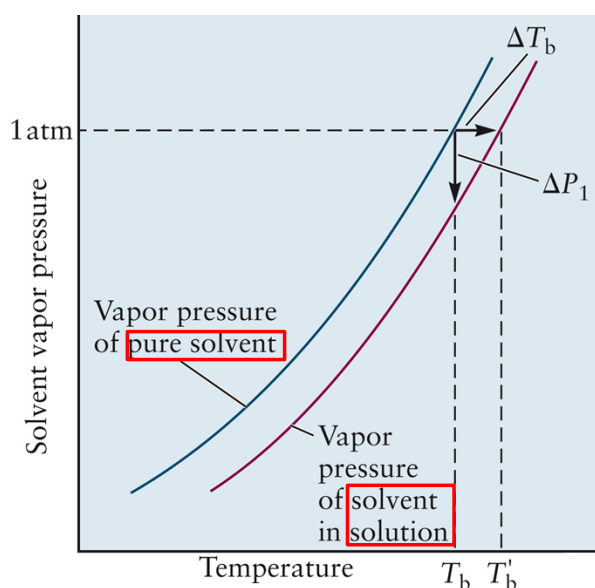


Fig. 11.11 Boiling point elevation.

For small concentrations of nondissociating solutes

$$S = \frac{-\Delta P_1}{T'_b - T_b} = -\frac{\Delta P_1}{\Delta T_b}$$

Slope of curve for the pure solvent only

$$\Delta T_b = -\frac{\Delta P_1}{S} = \frac{X_2 P_1^\circ}{S} = \frac{1}{S} \left[ \frac{n_2}{n_1 + n_2} \right]$$

For very dilute solutions,  $n_1 \gg n_2$

$$\Delta T_b = \frac{1}{S} \frac{n_2}{n_1} = \frac{1}{S} \left[ \frac{m_2 / \mathcal{M}_2}{m_1 / \mathcal{M}_1} \right]$$

↑  
Molar mass

For very dilute solutions,

$$\Delta T_b = \frac{1}{S} \left[ \frac{m_2/M_2}{m_1/M_1} \right]$$

❖ **Ebullioscopic constant ( $K_b$ )**  
 ➔ **solvent property**

$$K_b = \frac{M_1}{S} \times \frac{1 \text{ kg}}{1000 \text{ g}}$$

$$\Delta T_b = K_b \left( \frac{m_2/M_2}{m_1/(1000 \text{ g kg}^{-1})} \right)$$

Molality (m)

$$\Delta T_b = K_b m$$

↓  
Solvent property

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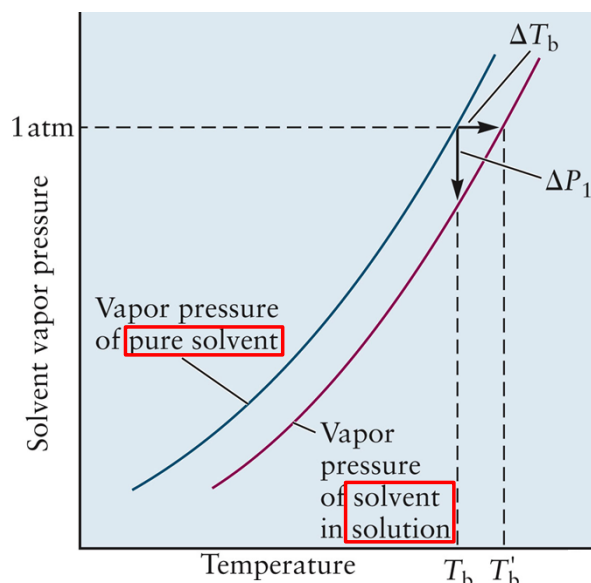


Fig. 11.11 Boiling point elevation.

$K_b = 0.512 \text{ K kg mol}^{-1}$  for water

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$K_b$  is obtained by measuring the boiling-point elevations for dilute solutions of known molality (that is, containing a known amount of solute with known molar mass).

TABLE 11.2

Boiling-Point Elevation and Freezing-Point Depression Constants

Solvent	Formula	$T_b$ (°C)	$K_b$ (K kg mol <sup>-1</sup> )	$T_f$ (°C)	$K_f$ (K kg mol <sup>-1</sup> )
Acetic acid	CH <sub>3</sub> COOH	118.1	3.07	17	3.9
Benzene	C <sub>6</sub> H <sub>6</sub>	80.1	2.53	5.5	4.9
Carbon tetrachloride	CCl <sub>4</sub>	76.7	5.03	-22.9	32
Diethyl ether	C <sub>4</sub> H <sub>10</sub> O	34.7	2.02	-116.2	1.8
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	78.4	1.22	-114.7	1.9
Naphthalene	C <sub>10</sub> H <sub>8</sub>	—	—	80.5	6.8
Water	H <sub>2</sub> O	100.0	0.512	0.0	1.86

Solvent property

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## How to make a delicious Ramyeon!



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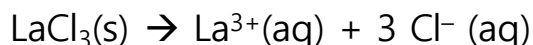
### EXAMPLE 11.12

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- (a) When 5.50 g of biphenyl ( $C_{12}H_{10}$ ) is dissolved in 100.0 g of benzene, the boiling point increases by  $0.903^\circ\text{C}$ . Calculate  $K_b$  for benzene.
- (b) When 6.30 g of an unknown hydrocarbon is dissolved in 150.0 g of Benzene, the boiling point of the solution increases by  $0.597^\circ\text{C}$ . What is the molar mass of the unknown substance?

### EXAMPLE 11.13

Lanthanum(III) chloride ( $\text{LaCl}_3$ ) is a salt that completely dissociates into ions in dilute aqueous solution,



Yielding 4 mol of ions per mole of  $\text{LaCl}_3$ . Suppose 0.2453 g of  $\text{LaCl}_3$  is dissolved in 10.00 g of  $\text{H}_2\text{O}$ . What is the boiling point of the solution at atmospheric pressure, assuming ideal solution behavior?

### ➤ Freezing-Point Depression

$$\Delta T_f = T'_f - T_f = -K_f m$$

$K_f$ : cryoscopic constant

$K_f = 1.86 \text{ K kg mol}^{-1}$  for water

For dissociating solutes,  
count total molalities.

$\text{Ca}(\text{NO}_3)_2$  total 3 moles  
( $\text{Ca}^{2+}$ ,  $2 \text{NO}_3^{-}$ 's)

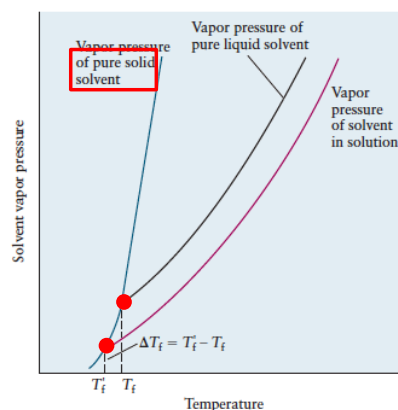
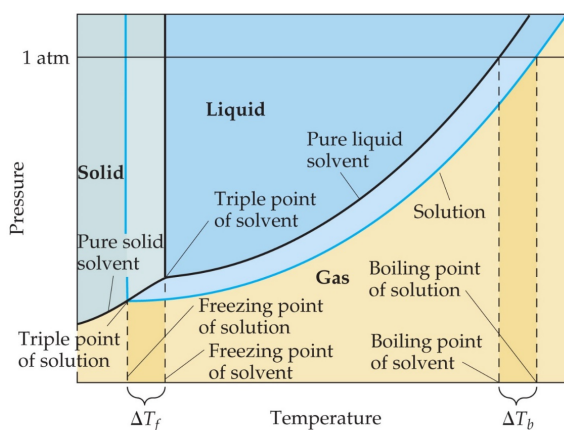


Fig. Freezing-point depression

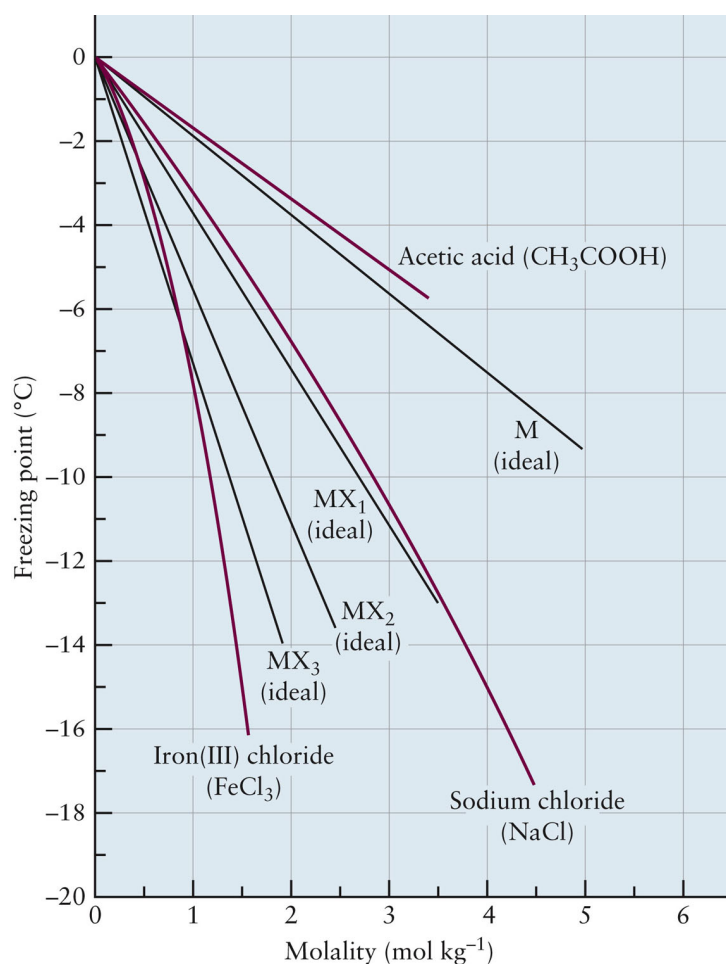




### EXAMPLE 11.15

When 0.494 g of  $\text{K}_3\text{Fe}(\text{CN})_6$  is dissolved in 100.0 g of water, the freezing point is found to be  $-0.093^\circ\text{C}$ . How many ions are present for each formula unit of  $\text{K}_3\text{Fe}(\text{CN})_6$  dissolved, assuming  $K_f = 1.86 \text{ K kg/mol}$  for water?

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**Fig. 11.13** Freezing-point depression of ionic substances.

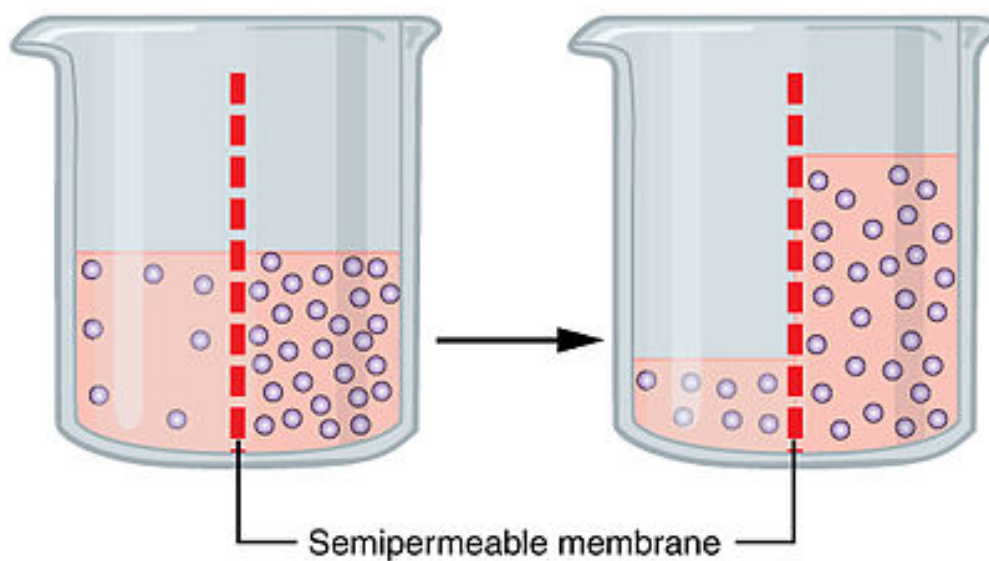
$\text{HAc}(\text{M})$ ,  $\text{NaCl}(\text{MX})$ ,  $\text{FeCl}_3(\text{MX}_3)$

As the molalities of the solutions increases, the observed freezing-point depressions deviate in varying ways from the straight lines.



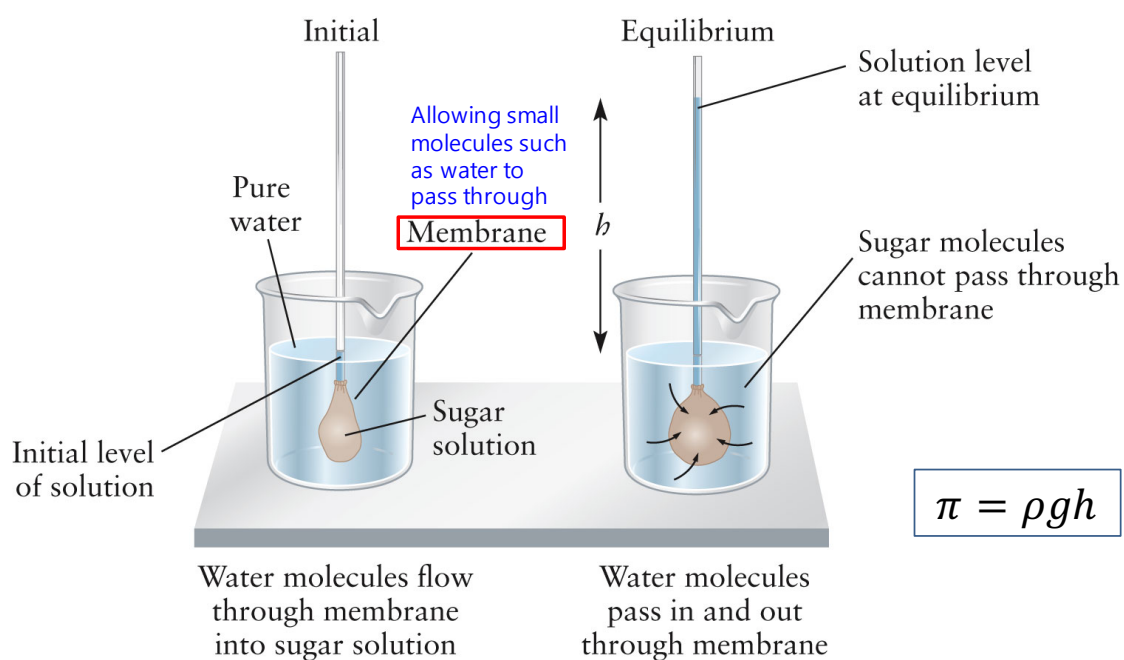


## ➤ Osmosis



[https://www.youtube.com/watch?v=w3\\_8FSrqc-l](https://www.youtube.com/watch?v=w3_8FSrqc-l)

## ➤ Osmosis



**Fig. 11.14** Measurement of the osmotic pressure.

## ➤ Osmosis

**Osmosis** is the movement of **solvent** particles **from a region of lower to a region of higher concentration** through a semi-permeable membrane. (Larger solute molecules can not pass through the membrane.)

**Osmotic pressure,  $\pi$** , is the pressure that must be applied to prevent the net flow of solvent.

van't Hoff equation

$$\pi = cRT$$

$$\pi V = nRT$$

$c$  = molarity =  $(n/V)$

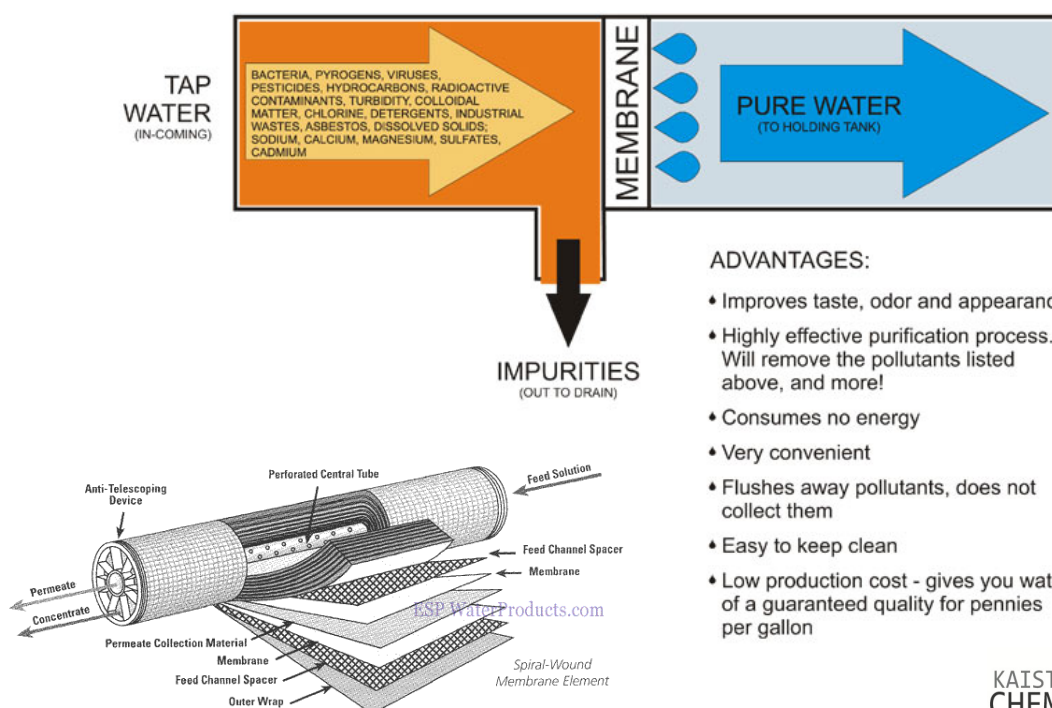
$R$  = 0.0821 atm·L/mol·K

$T$  = Kelvin temperature

The molar mass of a dissolved substance can be determined from the osmotic pressure of its solution.

## Reverse Osmosis

### FROM TAP WATER TO PURE WATER



**EXAMPLE 11.16**

A chemist dissolves 2.00 g of a protein in 0.100 L water. The osmotic pressure is 0.021 atm at 25°C. What is the approximate molar mass of the protein?

Osmotic pressure is useful for large molecules with low solubilities.

Under the identical conditions,

Osmotic pressure with  $h = 22 \text{ cm}$

Vapor-pressure lowering =  $4.8 \times 10^{-7} \text{ atm}$

Boiling-point elevation = 0.00044 K

Freezing-point depression = 0.0016 K

## 11.6 PHASE EQUILIBRIUM IN SOLUTIONS: VOLATILE SOLUTES

Two or more components, each of which is volatile.

Ideal mixture of volatile substances

$$P_1 = X_1 P_1^\circ, \quad P_2 = X_2 P_2^\circ = (1 - X_1) P_2^\circ$$

### ➤ Henry's Law

For  $X_2 \ll 1$ ,  $P_2 = k_2 X_2$

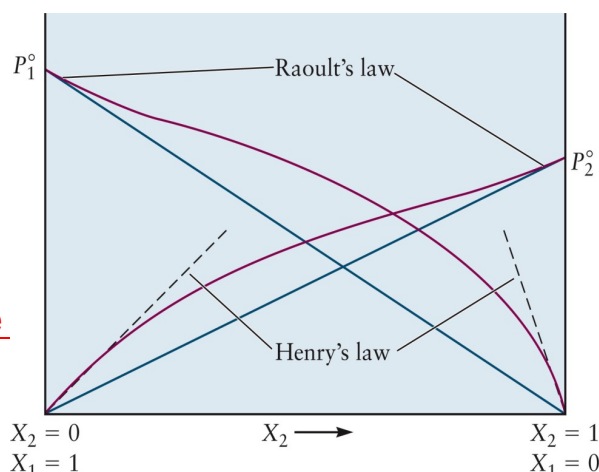
$k_2$ : Henry's law constant

For  $X_1 \ll 1$ ,  $P_1 = k_1 X_1$

~ Henry's law applies to a volatile solute in a dilute solution.

~ Carbonation of soft drinks

~ O<sub>2</sub> dissolved in blood



**Fig. 11.15** Vapor pressures above a mixture of two volatile liquids.

### ➤ Raoult's law

The **solvent** vapor pressure changes with the composition of the solution at a fixed temperature.

$P_1^\circ$  : vapor press of pure **solvent**

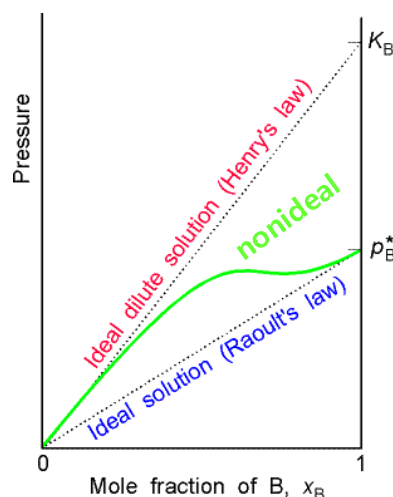
$$P_1 = X_1 P_1^\circ$$

### ➤ Henry's Law

For  $X_2 \ll 1$ ,  $P_2 = k_2 X_2$

$k_2$  : Henry's law constant

~ Henry's law applies to a volatile solute in a dilute solution.



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#### EXAMPLE 11.17

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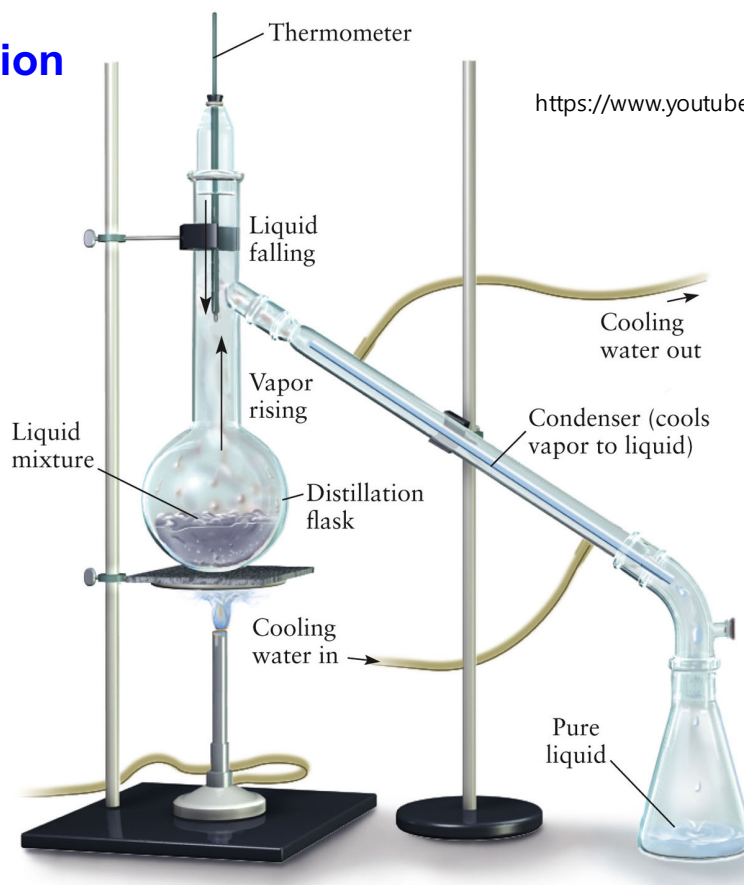
The Henry's law constant for **oxygen** dissolved in water is  $4.34 \times 10^4 \text{ atm}$  at  $25^\circ\text{C}$ . If the partial pressure of oxygen in air is  $0.20 \text{ atm}$  under ordinary atmospheric conditions, calculate the concentration (in moles per liter) of dissolved oxygen in water that is in equilibrium with air at  $25^\circ\text{C}$ .

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## ➤ Distillation

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<https://www.youtube.com/watch?v=0x2-8dedmE4>

**Fig. 11.18** An apparatus for fractional distillation.



## ➤ Distillation

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$P_1^\circ = 0.198 \text{ atm}$  for hexane ( $\text{C}_6\text{H}_{14}$ ) at  $25^\circ\text{C}$ .

$P_2^\circ = 0.0600 \text{ atm}$  for heptane ( $\text{C}_7\text{H}_{16}$ ) at  $25^\circ\text{C}$ .

A solution of  $n_1 = 4.00 \text{ mol}$  and  $n_2 = 6.00 \text{ mol}$ .

### ❖ Mole fractions in the **solution**

$$X_1 = 0.400, X_2 = 0.600$$

$$P_1 = X_1 P_1^\circ = (0.400)(0.198 \text{ atm}) = 0.0792 \text{ atm}$$

$$P_2 = X_2 P_2^\circ = (0.600)(0.0600 \text{ atm}) = 0.0360 \text{ atm}$$

$$P_{\text{tot}} = P_1 + P_2 = 0.1152 \text{ atm}$$

### ❖ Mole fractions in the **vapor** (Dalton's law)

$$P_1 = X_1' P_{\text{tot}}, P_2 = X_2' P_{\text{tot}}$$

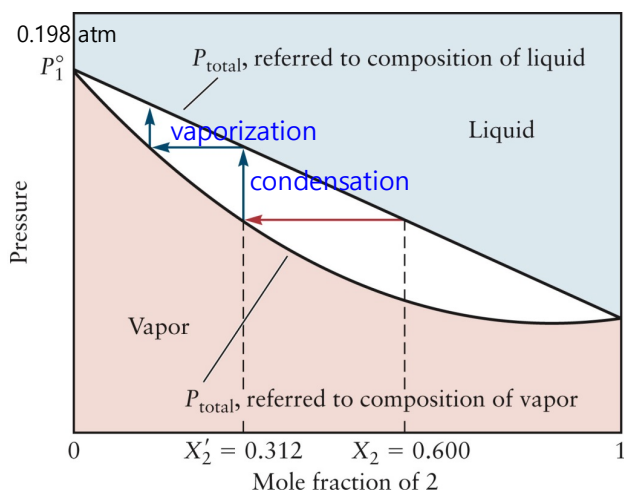
$$X_1' = 0.0792 \text{ atm} / 0.1152 \text{ atm} = 0.688$$

$$X_2' = 1 - X_1' = 1 - 0.688 = 0.312$$

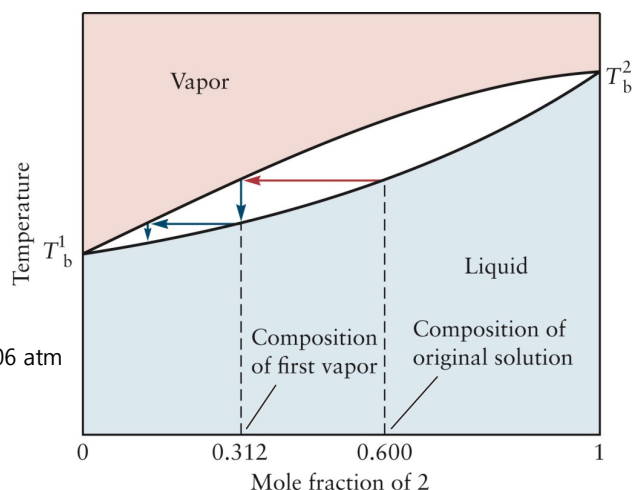
The liquid and the vapor with which it is in equilibrium have different compositions.

## ➤ Fractional Distillation

- ~ Separation of two or more components of a liquid solution by successive evaporation and condensation on the basis of their different boiling points
- ~ Some of vapor is removed and condensed to become liquid.



**Fig. 11.16** Vapor pressure vs.  $X_2$ .



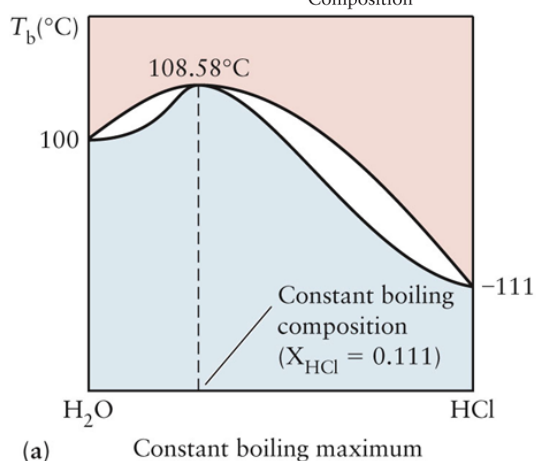
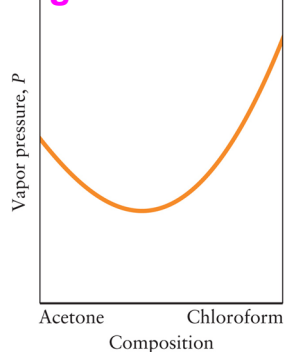
**Fig. 11.17** Boiling temperature vs.  $X_2$ .

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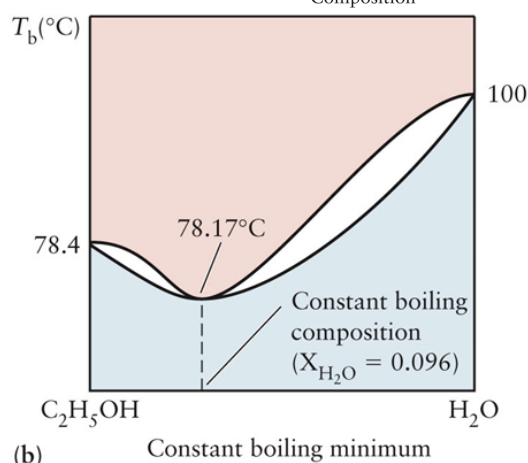
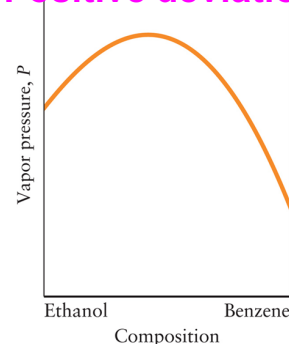
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## ◆ Azeotropes

Negative deviation

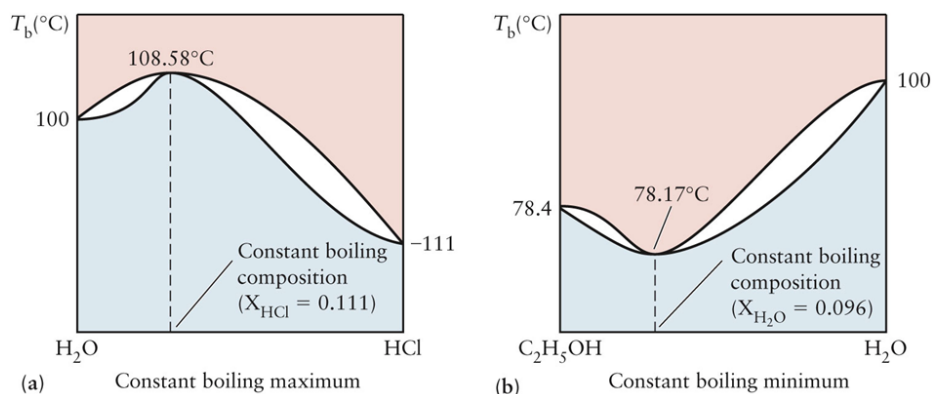


Positive deviation



**Fig. 11.19** (a) Maximum-boiling azeotrope. (b) Minimum-boiling azeotrope.

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➤ Maximum-boiling azeotrope

HCl / H<sub>2</sub>O

~ large negative deviation,  
strongly attractive b/w HCl & H<sub>2</sub>O

~  $T_b = 108.58^\circ\text{C}$  at  $X_{\text{HCl}} = 0.111$

➤ Minimum-boiling azeotrope

C<sub>2</sub>H<sub>5</sub>OH / H<sub>2</sub>O

~ large positive deviation (less  
attractive)

~  $T_b = 78.17^\circ\text{C}$  at  $X_{\text{H}_2\text{O}} = 0.096$

~ the last 4% of water **can not**  
**be** removed by distillation

An azeotrope behaves like a single-component fluid.

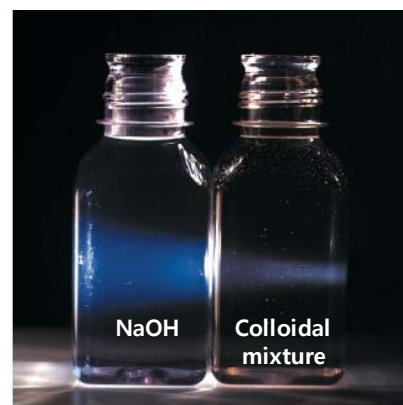
## 11.7 COLLOIDAL SUSPENSIONS

### ◆ Colloids

- A dispersion of large particles (1 nm ~ 1 μm) in a solvent
- Intermediate between a solution and a heterogeneous mixture
- Homogenous appearance but scatters light

Dispersed phase	Dispersion medium	Technical name	Examples
solid	gas	aerosol	smoke
liquid	gas	aerosol	hairspray, mist, fog
solid	liquid	sol or gel	printing ink, paint
liquid	liquid	emulsion	milk, mayonnaise
gas	liquid	foam	fire-extinguisher foam
solid	solid	solid dispersion	ruby glass (Au in glass); some alloys
liquid	solid	solid emulsion	bituminous road paving; ice cream
gas	solid	solid foam	insulating foam

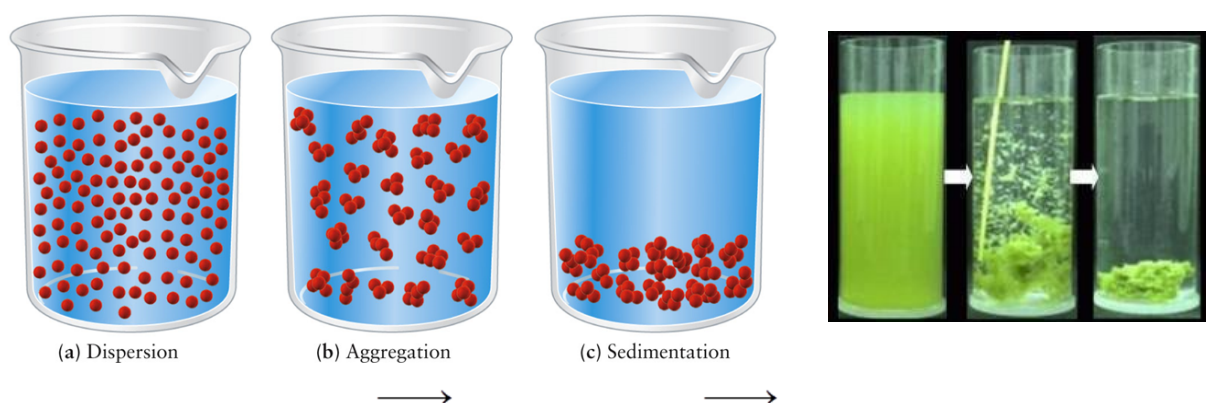
\*Based on R. J. Hunter, *Foundations of Colloid Science*, Vol. 1 (Oxford: Oxford University Press, 1987).





## ➤ Flocculation

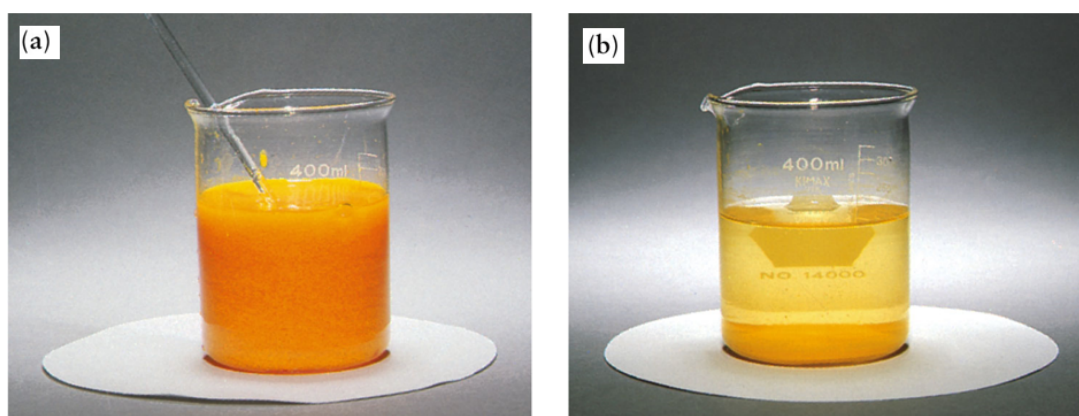
- ~ Acceleration of the settling out of a colloid through the addition of salts.
- ~ Salts **reduce** the electrostatic repulsions between suspended particles. (ex. river deltas, paints)



**Fig. 11.21** Process of flocculation: Dispersion → Aggregation → Sedimentation  
General Chemistry I

## ➤ Precipitation

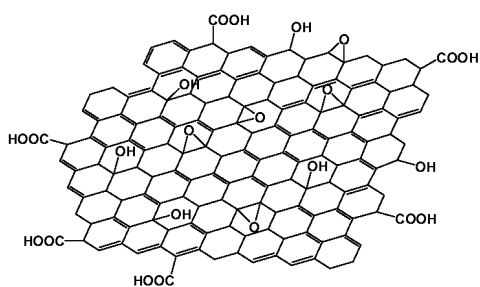
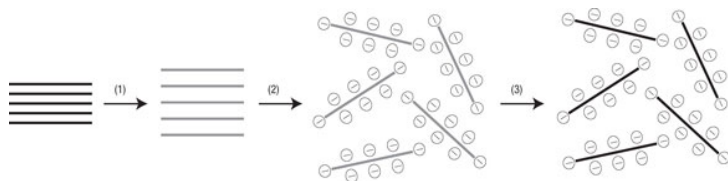
- ~ flocculation, centrifugation, membrane filtration



**Fig. 11.22** (a) This colloidal suspension of  $\text{PbCrO}_4$  appears cloudy.  
(b) After flocculation, the precipitate settles to the bottom.

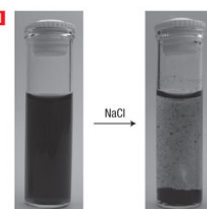
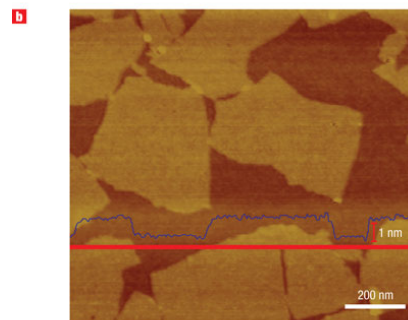
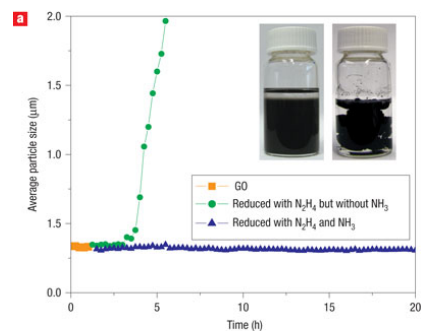
## Processable aqueous dispersions of graphene nanosheets

Nature Nanotechnology 3, 101-105 (2008)



Formula I

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## 10 Problem Sets

For Chapter 11,

3, 13, 18, 25, 34, 43, 55, 62, 72, 83

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