Mixtures

What happens to the properties (phase changes)
when we make a solution?

Let's look at the following "reaction"

water + salt ------> "salt water"

Which has the higher entropy?

A.   The water + the solid salt

B.   The solution ⟵

C.   They are exactly the same

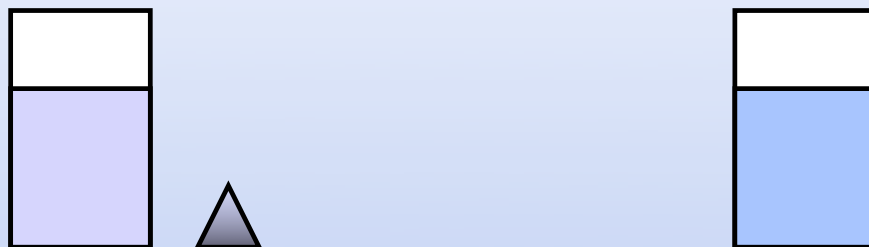Let's look at the following "reaction"

water + salt ------> "salt water"

Which has the higher enthalpy?

A. The water + the solid salt

B. The solution

C. They are essentially the same ⟵

Let's look at the following "reaction"

water + salt ------> "salt water"

Which has the lower free energy?

A.   The water + the solid salt

B.   The solution   ⟵

C.   They are exactly the same

This is an ideal solution

$\Delta G_{solution} < 0$

because

$\Delta S_{solution} > 0$

and $\Delta H_{solution} = 0$

ITS ALL THE ENTROPY!!

This is an approximation. But if we look at mixtures
that are easily formed (like + like) then it isn't bad

Demo

What is the **key** effect of adding the salt to the water?

A.   the salt dissolving is endothermic so the temperature drops

B.   the salt dissolving is exothermic so it melts the ice

C.   the salt dissolving increases the entropy of the solution

D.   the salt dissolving increases the entropy of the solid ice
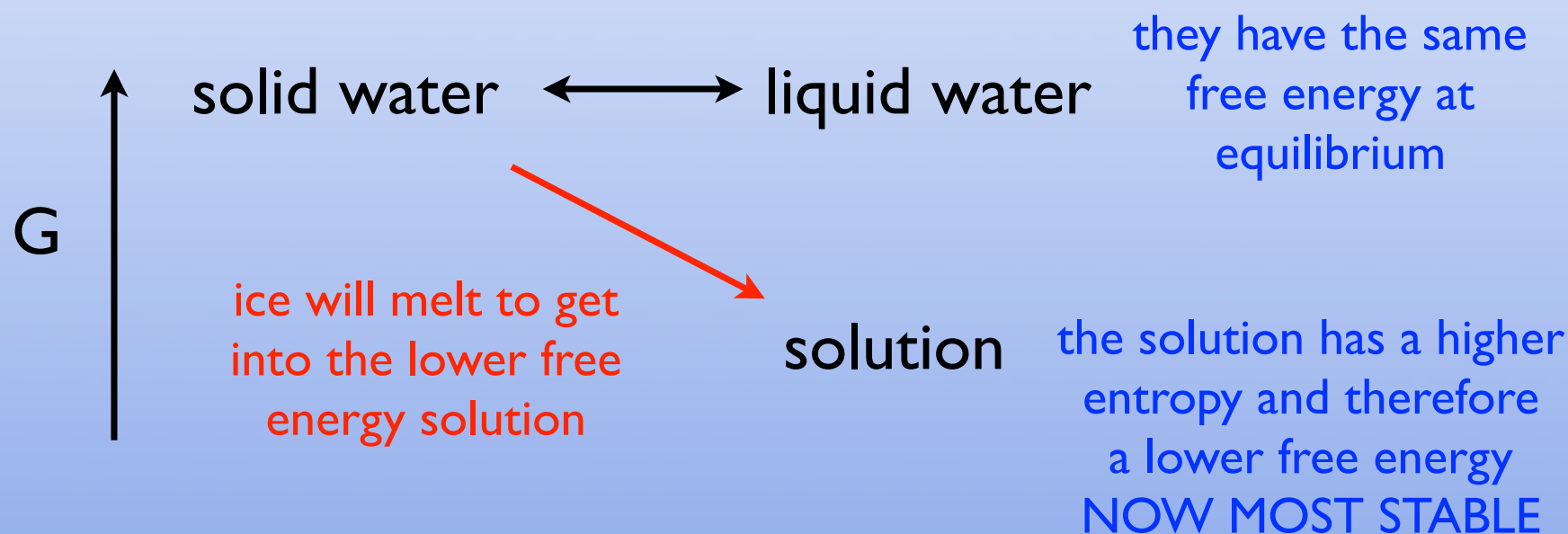
Why does the temperature drop?

A. the salt dissolving requires energy (endothermic)

B. the salt dissolving releases energy (exothermic)

C. the ice melting releases energy (exothermic)

D. the ice melting requires energy (endothermic)

Solutions

The main effect of making a solution is that the entropy of the solution is higher than the separate solvent and solute

T = 0°C and P = 1 atm
Let's compare the energy of the liquid and solid

G

solid water ⟷ liquid water

they have the same free energy at equilibrium

ice will melt to get into the lower free energy solution

solution

the solution has a higher entropy and therefore a lower free energy
NOW MOST STABLE

There will be a number of effects that are all the same

When we make a solution

its entropy increases

therefore its free energy decreases

therefore it is more STABLE than the pure liquid

There will be a number of effects that are all the same

The liquid solution is now more stable!

Therefore it will remain liquid
over a larger temperature range

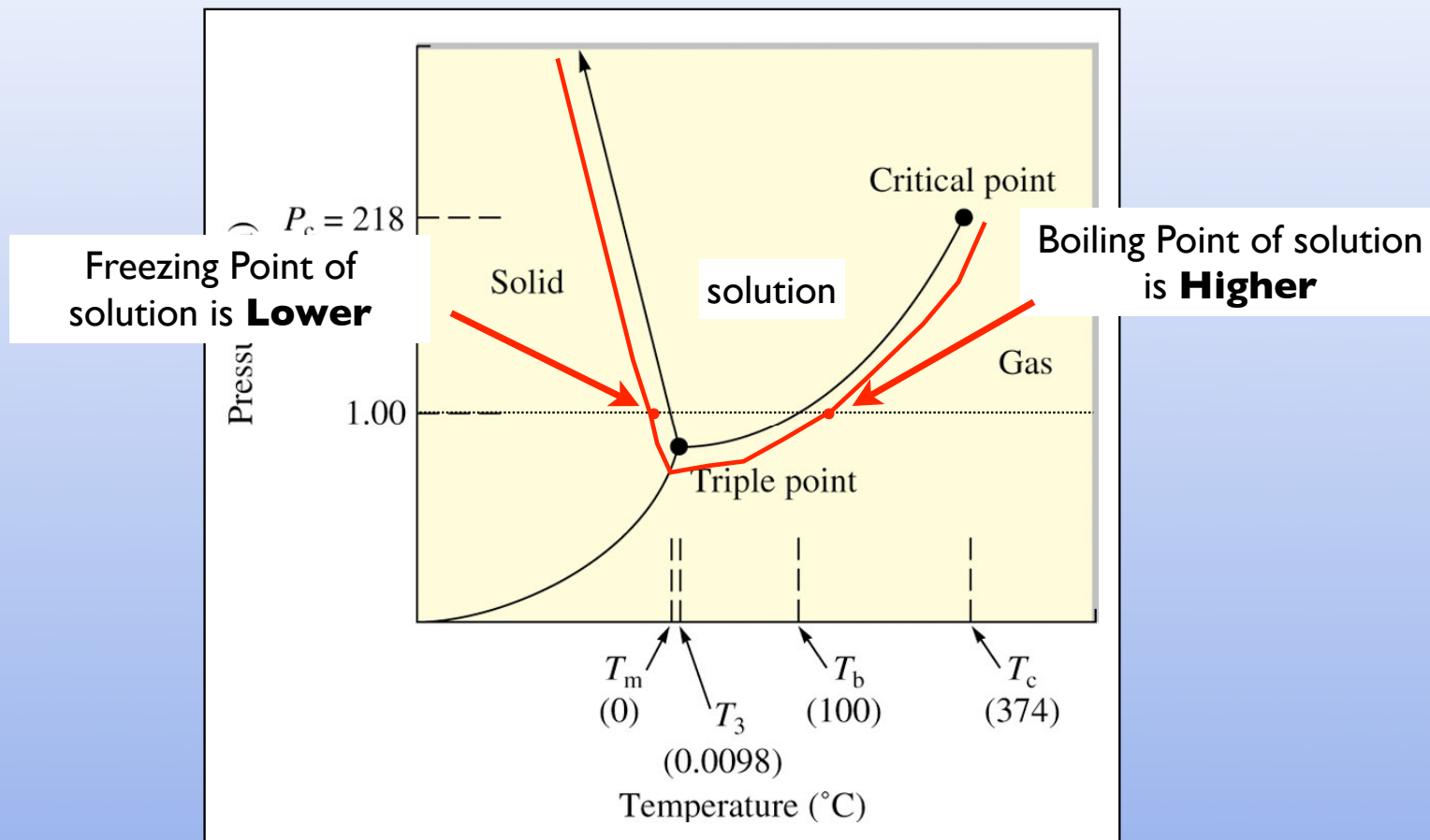"harder" to freeze
Freezing point depression

"harder" to boil
Boiling point elevation

Only the liquid phase is a mixture
The solid and the gas are still pure solvent

Phase Diagram for Water
Phase Diagram for a water solution

Freezing Point of solution is **Lower**

Boiling Point of solution is **Higher**

$P_c = 218$

Critical point

Solid

solution

Gas

1.00

Pressure

Triple point

T_m (0)

T_3 (0.0098)

T_b (100)

T_c (374)

Temperature (°C)

This effect depends on the entropy of the
solution which depends on how much "stuff"
is dissolved but not what the "stuff" is

Colligative Properties
depend on the concentration of the solution
but not what is actually dissolved
(note: this is approximate as it assumes and
ideal solution)

The only thing that matters is the number of
moles of "stuff"

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Different ways to describe concentration

All of them are essentially

$$\frac{\text{Amount of solute}}{\text{Amount of everything (solvent)}}$$

Mole Fraction

$$\chi_i = \frac{\text{moles of i}}{\text{total moles}}$$

Molality

$$m = \frac{\text{moles of solute}}{\text{kg of solvent}}$$

Molarity

$$M = \frac{\text{moles of solute}}{\text{L of solution}}$$

What matters is the number of moles
that are not the solvent

Molecular materials

1 M sugar solution = 1 moles of sugar in 1 L solution
1 mole of "stuff"

Ionic materials

1 M NaCl solution = 1 moles of Na^+ in 1 L solution
1 mole of Cl^- in 1 L solution

2 moles of "stuff"

Van't Hoff Number

$$i = \frac{\text{moles of "particles" in solution}}{\text{moles of solute dissovled}}$$

TABLE 17.6 Expected and Observed Values of the van't Hoff Factor for 0.05 *m* Solutions of Several Electrolytes

Electrolyte	i (expected)	i (observed)
NaCl	2.0	1.9
$MgCl_2$	3.0	2.7
$MgSO_4$	2.0	1.3
$FeCl_3$	4.0	3.4
HCl	2.0	1.9
Glucose*	1.0	1.0

*A nonelectrolyte shown for comparison.

Sometimes the ions in solution "pair"

and the effective concentration

is lower than the expected concentration

Effect of making the solution

Boiling Point Elevation

Solution now more stable than vapor. Therefore the boiling point goes up

Freezing Point Depression

Solution now more stable than solid. Therefore the freezing point goes down

constant that depends on solvent

Boiling Point Elevation

$$\Delta T = K_b m_{solute}$$

molality solute

Remember the number of particles is what matters

$$\Delta T = i K_b m_{solute}$$

van't Hoff number

constant that depends on solvent

Freezing Point Depression $\qquad \Delta T = -K_f m_{solute}$

molality solute

Remember the number of particles is what matters

$$\Delta T = -i K_f m_{solute}$$

van't Hoff number

TABLE 17.5 Molal Boiling-Point Elevation Constants (K_b) and Freezing-Point Depression Constants (K_f) for Several Solvents

Solvent	Boiling Point (°C)	K_b (°C kg/mol)	Freezing Point (°C)	K_f (°C kg/mol)
Water (H_2O)	100.0	0.51	0.	1.86
Carbon tetrachloride (CCl_4)	76.5	5.03	−22.99	30.
Chloroform ($CHCl_3$)	61.2	3.63	−63.5	4.70
Benzene (C_6H_6)	80.1	2.53	5.5	5.12
Carbon disulfide (CS_2)	46.2	2.34	−111.5	3.83
Ethyl ether ($C_4H_{10}O$)	34.5	2.02	−116.2	1.79
Camphor ($C_{10}H_{16}O$)	208.0	5.95	179.8	40.

Note: sometime K_f is given as negative. You must keep this straight. Freezing point goes down. Boiling point goes up. Adapt the formula to make it work

Principles of Chemistry II

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Which would you expect to have the lowest freezing point

A.   2 M sugar solution
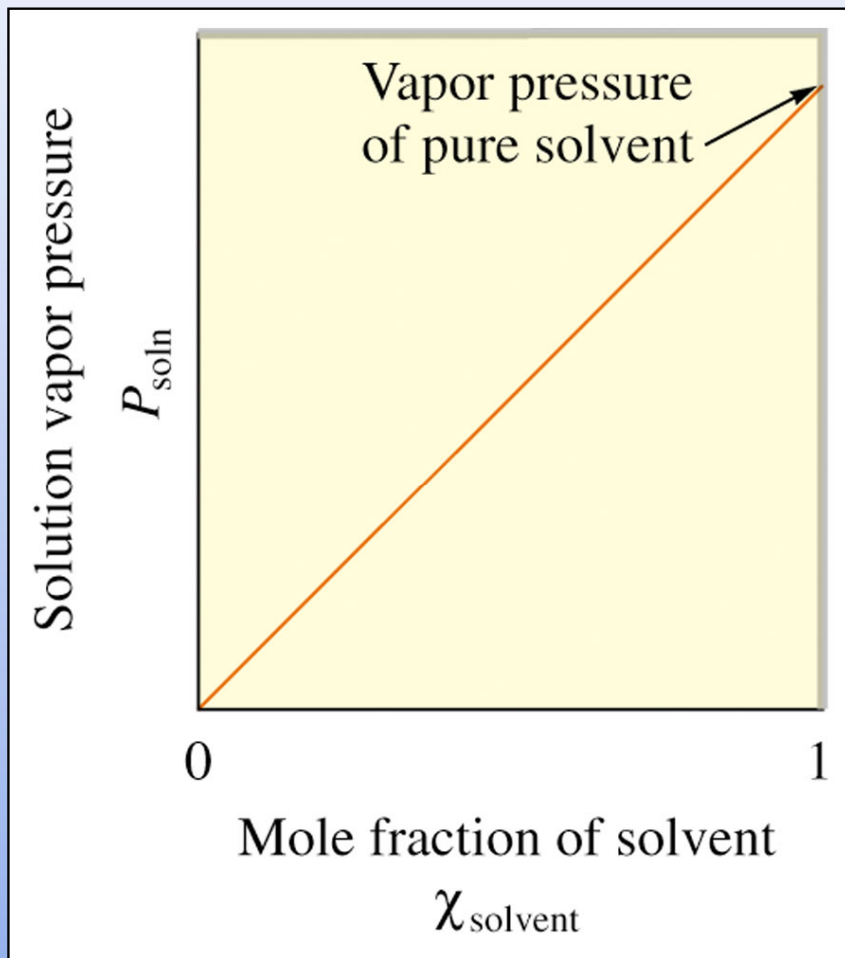
B.   0.5 M NaCl solution

C.   1 M NaCl solution

D.   1 M MgCl$_2$ solution ⟵

If the boiling point is higher,
what is the vapor pressure of the solution?

A.   higher than the pure solvent

B.   lower than the pure solvent ←——————————

C.   the same as the pure solvent
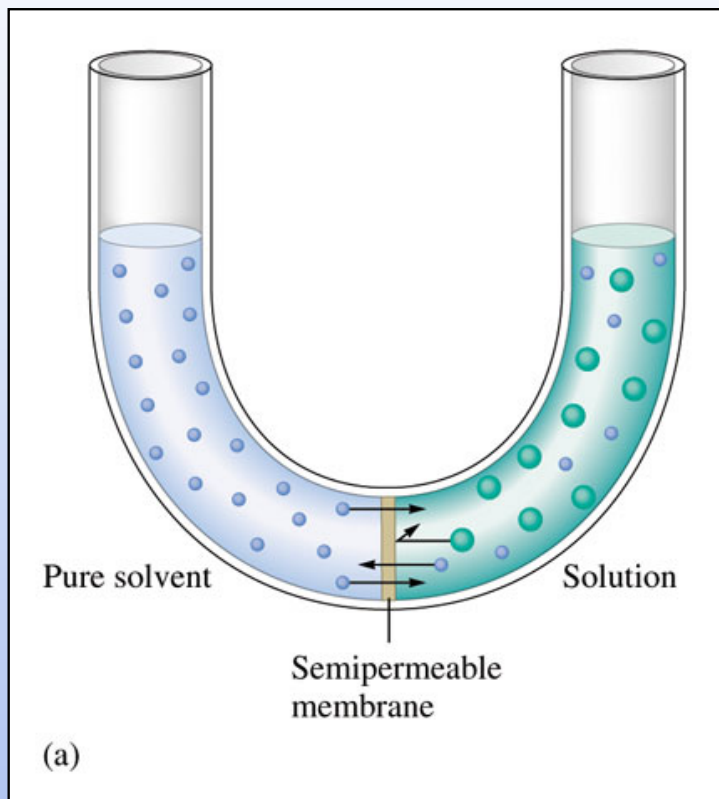
Raoult's Law

vapor pressure of pure solvent

$$P_{solvent} = X_{solvent}P°$$

mole fraction of solvent!

Just like Henry's Law

But the constant
is the pure vapor pressure!

Osmosis

Pure solvent
Solution
Semipermeable membrane
(a)
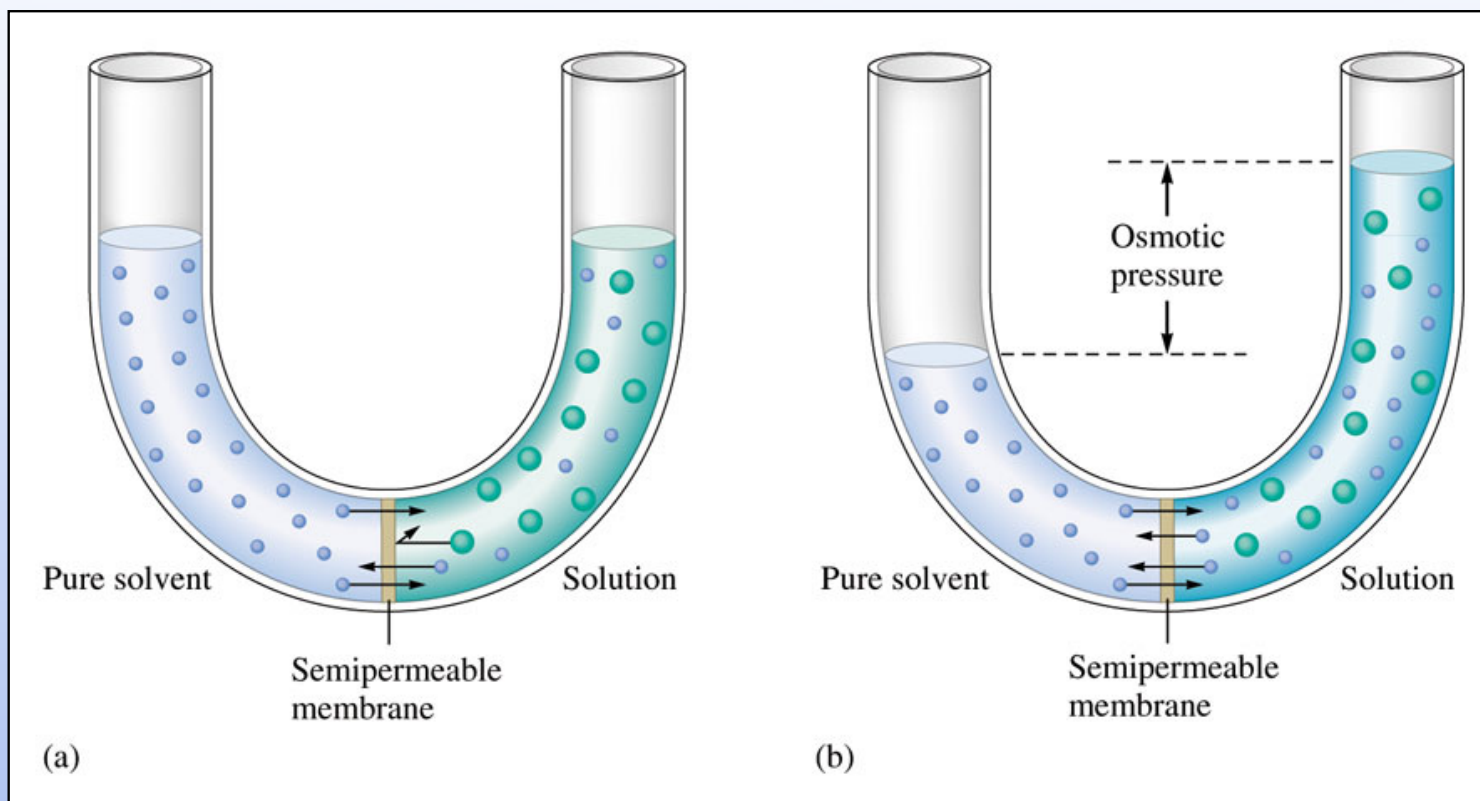
Which side has the lower free energy?

A. The solution

B. The pure solvent

C. They are the same

D. It depends on T

Two liquids separated by a membrane
Solvent can pass through the membrane
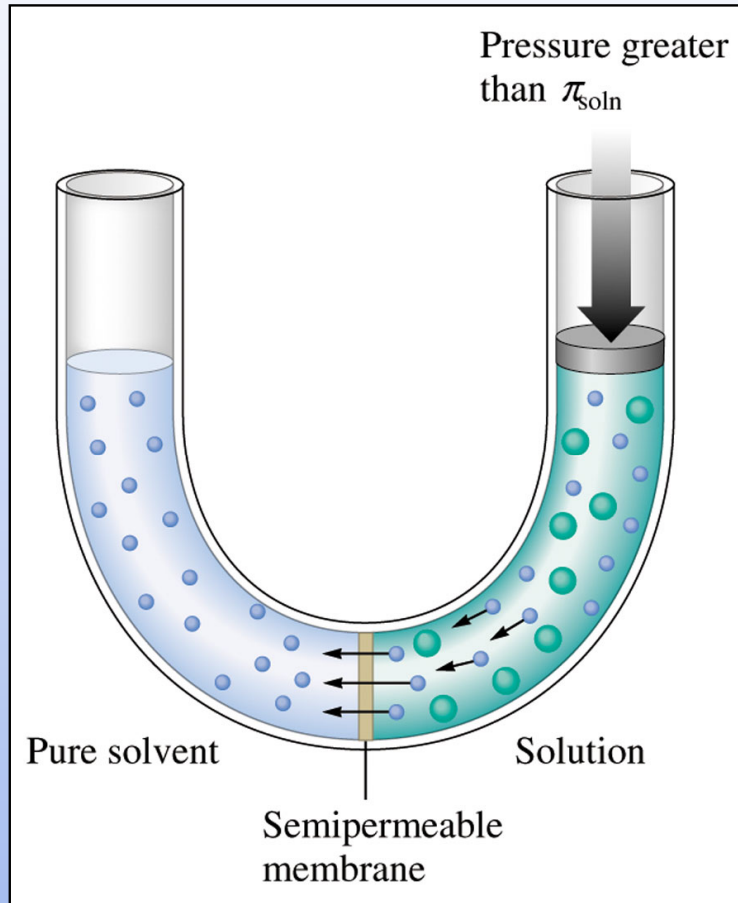but the solute can't pass through

Osmosis

The solvent will move to the solution side
to lower its free energy!
(at some point it will stop due to gravity
difference in height = difference in pressure)
once it stops, they have the same free energy (that is why it stops)

Reverse Osmosis

Pressure greater than π_{soln}

Pure solvent

Solution

Semipermeable membrane

Which side has the lower free energy?

A. The solution

B. The pure solvent

C. They are the same

D. It depends on T

They are now the same.
Solution has higher entropy (it is mixed up) but it has a higher enthalpy (they molecular are being forced together at higher P!)

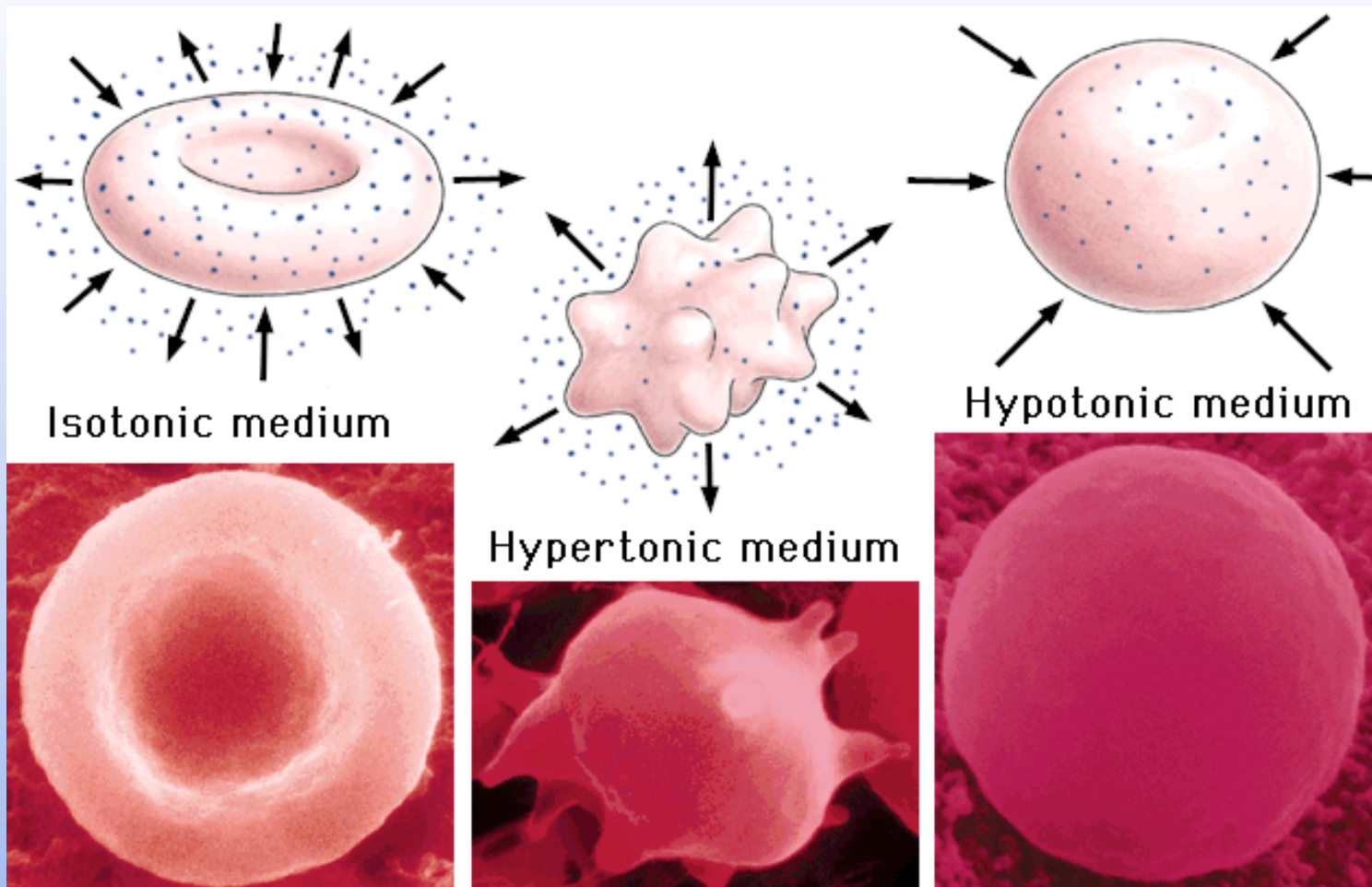this is just like before, but the pressure is not a result of the gravity

Osmotic Pressure

$$\Pi = MRT$$

Osmotic pressure

Molarity of solution!

$$\Pi = iMRT$$

Cells

Isotonic medium

Hypertonic medium

Hypotonic medium

Concentration of solution same as in the cell

Concentration of solution higher than in the cell

Concentration of solution lower than in the cell