Colligative Properties (Sect. 8.14-8.17)

- By definition a colligative property is a solution property (a property of mixtures) for which it is the amount of solute dissolved in the solvent matters but the kind of solute does not matter.

- Coming to grips with this concept should immediately remind you of kinetic molecular theory of gases—in that case we treated gas molecules as indistinguishable hard spheres and (ideally) it was the number of them, rather than the type of molecules, that determined gas properties.

- This means that when considering the impact of solute on a colligative property,

  1 mole of sugar ≡ 1 mole Na^+ ≡ 1 mole O^{2-} ≡ 1 mole urea ≡ 1 mole pickles do exactly the same thing

Listed below are the four colligative properties we will examine during this lecture—each is kind of fun because it is associated with fairly famous physical phenomena that you might like to explain to a friend .

Colligative Properties

◆Vapor Pressure Lowering—explains the value of putting antifreeze in your radiator to keep a car from overheating

◆Boiling Point Raising—explains how you can cook spaghetti faster in salt water

◆Freezing Point Lowering explains why salt is placed on roads to keep ice from forming

◆Osmotic Pressure explains why your little brother killed the family fish when he placed them in pure water while cleaning the tank.

For each of these properties you will be introduced to the physical phenomenon behind the property and learn how to perform simple calculations to determine the magnitude the change in solution state function associated with a colligative property.

Concentration and Colligative Properties

If colligative properties depend on the amount of the solute in the solvent, then the equations defining them must include a concentration term, and sure enough, they do. Over the next few pages you will be introduced to the equations in the context of the specific properties, but for now, simply note the similarities in structure for the equations: each equation includes a colligative property on the left side of the equation that is set equal to a concentration term and a solvent constant.

ΔP vapor pressure ΔT temperature raising or lowering π osmotic pressure

$$\Delta T_f = -mK_f$$

$$\Delta P = \chi P^0 \qquad \Delta T_f = -mK_f \qquad \pi = MRT$$

Three properties set equal to three different concentrations terms times a solvent constant

Let's practice performing concentration calculations. Two of these, molarity, M, and mole fraction, X, should be familiar to you. A third, molality, m, may be new. But all are useful ways to define the amount of stuff in solution—the more stuff, the larger the concentration.

Let's start by imagining that we are placing 50 g (0.146 mole) of the solute, sugar, in 117 g (6.5 mole) of the solvent, H_2O.

♦What is χ (mole fraction) of 50g of sugar in 117 g of water?

$$\chi = \frac{molesA}{molesA + molesB} = \frac{0.146sugar}{0.146sugar + 6.5H_2O} = \textbf{0.022 mole fraction sugar}$$

♦What is m (molality) of 50g of sugar in 117 g of water? Note that the moloaity calculation is similar to a molarity calculation except that we divide by the mass of the solvent in kg rather than the liters of solution.

$$m = \frac{molesA}{kg, solvent} = \frac{0.146mole, sugar}{0.117kg, H_2O} = \textbf{1.25 molal}$$

♦What is M (molarity) of 50g of sugar in 117 g of water? First we need to find the volume of solution from a density calculation.

$$V_{solution} = \text{(mass)(density)} = (50\text{ g} + 117\text{ g})\left(\frac{1mL}{1.34g}\right) = 125\text{ mL}$$

$$M = \frac{molesA}{V_{solution}} = \frac{0.146moles}{0.125L} = \mathbf{1.17\ Molar}$$

So we have 3 ways to describe 50g of sugar in 117 g of water, each of which is used in a colligative property calculation.

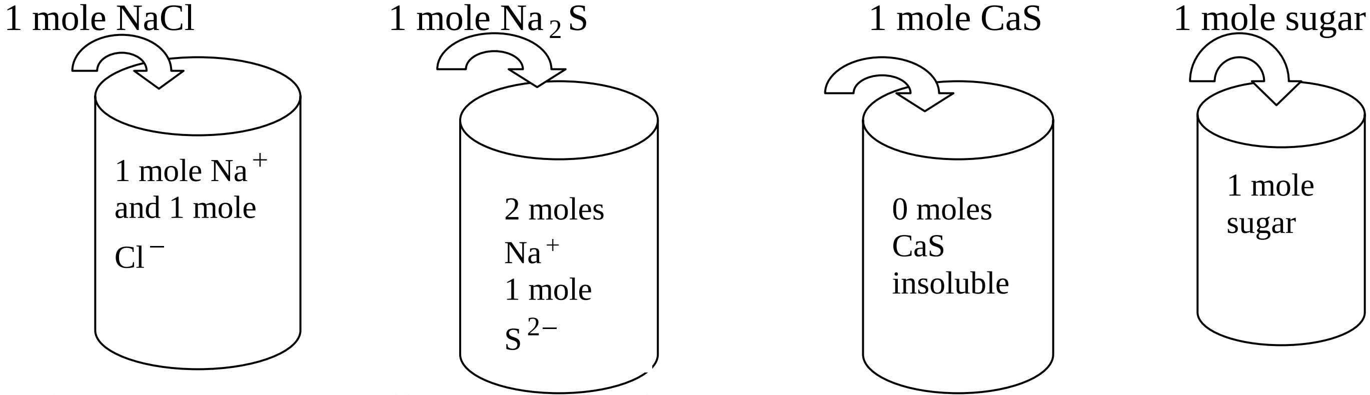
0.022 mole fraction ≡ 1.25 m ≡ 1.17 M

Time out for the Van’t Hoff equation.

Every test on colligative properties includes a question that employs the Van’t Hoff equation. Text books make this seem a lot harder than it is. Very simply, Van’t Hoff corrects for the fact that the number of particles you thrown into solution is not always the number of particles that determine the magnitude of the property. For example, think about what happens when you put the following one mole quantities into a liter of water. Which one raises the boiling point the most?

1. 1 mole NaCl **2.** 1 mole Na_2S **3.** 1 mole CaS **4.** 1 mole sugar

You might think 1 mole is 1 mole is 1 mole, and they are all the same. But



In fact each produces a different number of dissolved particles in solution.

- 1mole of NaCl is 2 moles of particles in the solvent
- 1 mole of Na_2S is 3 moles of particles in the solvent
- 1 mole of insoluble CaS is 0 moles of particles in the solvent
- 1 mole of sugar is 1 mole of particles in solution

What we need is a correction factor for each compound, ***i***, the Van’t Hoff factor, which is ***i*** = 2, 3, 0 and 1, respectively for the four solutions. ***i*** is simply inserted into every colligative property equation to make the correction.

Oh, and the answer to the original question about the change in boiling point for the four one mole samples?

1 mole Na_2S > 1 mole NaCl > 1 mole sugar > 1 mole CaS

So how big of an effect does a solute concentration have on a colligative property?

Now time for some math with the four different equations for colligative properties. Suppose we wanted to measure just how much 50 grams of sugar in 117 grams of water changed the magnitude of a state function.

Colligative property 1: Vapor pressure depression

$$\Delta P = P^0 \chi \longleftarrow \text{mole fraction which is the amount of solute added}$$

depression
in vapor pressure

constant which is the vapor pressure of pure solvent at a given T. of pure solvent

For H_2O at 25 ^oC the pure vapor pressure is 23.8 torr

So the vapor pressure depression in **ΔP = 23.8 torr (0.022) = 0.524 torr**

And the new vapor pressure is now about **23.3 torr.**

By the way, this equation is referred to as Raoult's Law which says simply that the vapor pressure above a solution is proportional to the mole fraction of the solute.

Time out for a famous vapor pressure calculation.

Calculating the total vapor pressure of a binary mixture of two volatile solvents.

Note that in the problem above, we determined the reduction in vapor pressure of the solvent. It decreased from 23.8 torr to 23.3 torr. But what if two volatile compounds were mixed together. Each would contribute to the other having a vapor pressure lowering, but the overall vapor pressure would have to be determined by adding together the individual vapor pressures of the two compounds.

Sample problem. Suppose you combine two compounds, A and B, in a mole ratio of 0.25 to 0.75. At a given temperature, the pure vapor pressure of compound A is 100 torr and the pure vapor pressure of compounds B is 50 torr. What are the new vapor pressures for A and B combined.

Calculation.

First, determine the vapor pressure for each compound:

For compound A-- $P_a = P_a^0 \chi$ = 100 torr x 0.25 = 25 torr contribution for A.

For compound B—$P_b = P_b^0 \chi$ = 50 torr x 0.75 = 37.5 torr contribution for B.

Total vapor pressure above the solution (assuming gas ideality and using Dalton’s Law of partial Pressures)

$P_{tot} = P_a + Pb = 25 + 37.5$ torr = 62.5 torr.

Note this problem can be made more complicated by making you work to calculate a mole fraction (I started by having a mole fraction.)

Colligative Property 2: boiling point elevation

$\Delta T_b = K_b m \longleftarrow$ molality which is the amount of solute added

temperature
increase because of solute

constant which is the boiling point elevation constant for water

For water, K_b is 0.512 ^oC/molal

So the boiling point elevation is **$\Delta T_b = K_b m = (0.512)(1.25\ m) = 0.64^o$**

And the new b.p. of water with a heck of a lot of sugar in it is **$100.64^o C$**

Colligative Property 3: freezing point depression

$\Delta T_f = K_f m \longleftarrow$ molality which is the amount of solute added

temperature
decrease because of solute

constant which is the boiling point elevation constant for water

For water, K_b 1.86 ^oC/molal

So the boiling point elevation is **$\Delta T_f = -K_f m = -(1.86)(1.25) = 2.32^o C$**

And the new f.p. of water with a heck of a lot of sugar in it is **$-2.32^o C$**

Colligative Property 4: osmotic pressure

$\pi = MRT$ ← molarity which is the amount of solute added

Osmotic pressure
increase because of solute

constant, RT, which seems to pop up everywhere

The constants R and T are the ideal gas law constant and the system temperature

So the osmotic pressure change is $\boldsymbol{\pi}$ = MRT = (1.17 M)(0.082)(298 K) = **28.6 atm**

Comparison of magnitudes of colligative property changes.

Let’s look at how much the colligative property change was for the same solute/solvent combination—note that what determines the magnitude of the overall change is the amplification by the constant term—in other words, the bigger the constant, the bigger the change, and the clear winner is the RT term for osmotic pressure. Sample values for freezing and boiling points constants for different solvents also give you an idea of what kind of changes to expect for different solvents.

- ΔP lowers water vapor pressure from 23.8 to 23.3 torr
- ΔT_b raises boiling point of water from 100^oC to 100.64^oC
- ΔT_f lowers freezing point of water from 0^oC to -2.32^oC
- π raises osmotic pressure from 1 atm to 28.6 atm

While the temperature was changing by a degree or so for boiling point elevation or freezing point depression, there was a near 30-fold increase in osmotic pressure—no wonder fish are so sensitive.

Not that even with small changes, significant impacts can occur in the real world, as we will see:

- Vapor pressure lowering explains why we add ethylene glycol to water.
- Boiling point elevation explains how adding salt to water speeds up cooking pasta.
- Freezing point depression explains how putting salt on icy roads melts ice.
- Osmotic pressure change explains lysing of cells or why you can’t put salt water fish in fresh water.

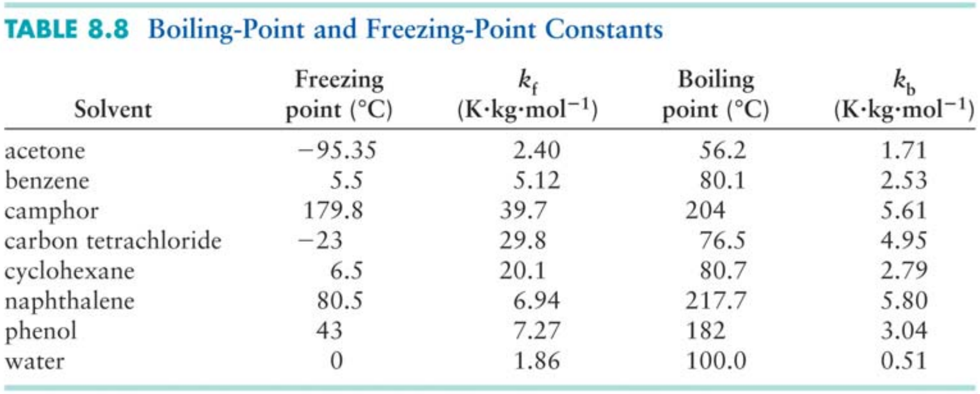


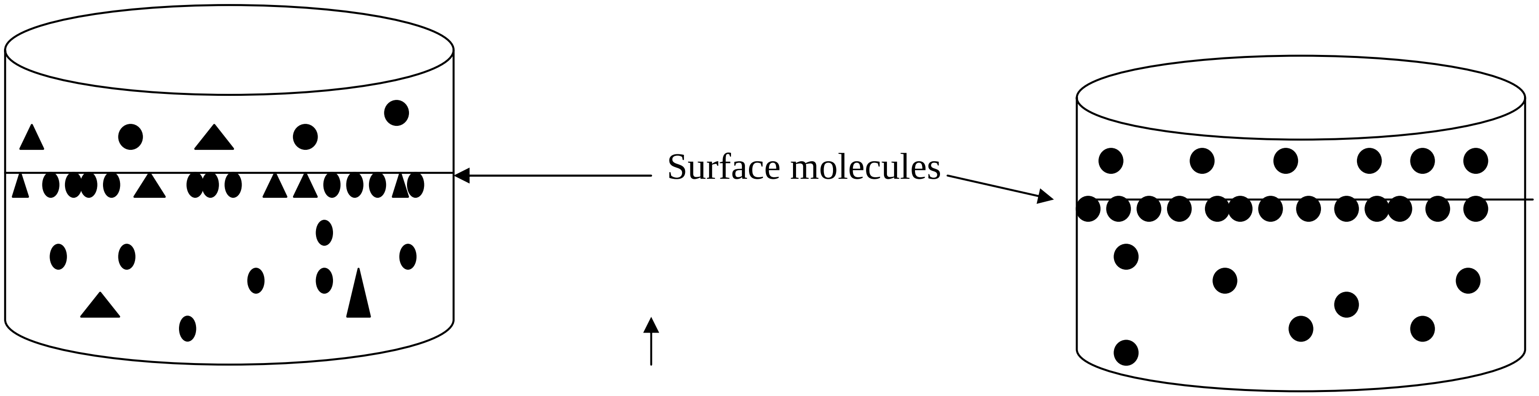
TABLE 8.8 Boiling-Point and Freezing-Point Constants

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

A bit of theory with bad pictures to explain colligative properties

Colligative property 1: Vapor pressure depression and boiling point elevation. What happens when ▲ you add to pure ● ? Look at the drawing below to see a simple explanation.

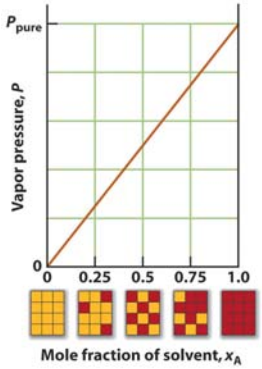
Mixture 75 % ● to 25% ▲ compared to Pure solution of 100% ●



$\Delta P = \chi P^0$ — 25% (χ), pure solvent (P^0)

$\Delta P = \chi P^0$ — 0% (χ), pure solvent (P^0)

Since we know that vapor pressure is a surface phenomenon, we see that one obvious reason for the reduction in vapor pressure is that there are fewer surface locations to put a molecule. So the solvent will have to have a reduction in vapor pressure because fewer molecules are present to leave the surface. The plot of mole fraction versus vapor pressure shows this obvious consequence.



A second reason for the reduction in vapor pressure is an entropic effect. Recall that highly ordered systems are not favored, and so for example, pure liquids will have a larger driving force from the change in entropy compared to mixtures which have a smaller entropy change.

Finally, note that the same argument that explains vapor pressure lowering also explains boiling point elevation. If the definition of boiling is that the vapor pressure exceeds atmospheric pressure, and the vapor pressure is lowered, then you need to raise temperature to achieve boiling.

Examples of vapor pressure lowering in action—your car radiator

While you may not know a lot about the car daddy bought you, one thing that would make sense is that you want the liquid in your radiator to remain a liquid. Turning into a solid at really cold temperature, or turning into a vapor at high temperature, probably isn't the best way to get the cooling action of recirculating fluid in a radiator going.

So what happens if you decide to use pure water as your radiator coolant:

	f.p.	b.p.
H_2O	0^o	100

Or maybe you gould use a different solvent like pure ethylene glycol—that green stuff you buy in stores.

	f.p.	b.p.
ethylene glycol	-12^o	135^o

Note that this isn't the greatest temperature range for people who live in Canada and vacation in Florida. Your car radiator can freeze or overheat pretty easily with these pure liquids. But what happens if we take advantage of vapor pressure lowering by creating a mixture of two solvents.

	f.p.	b.p.	
50-50 H_2O, E.G.	-34^o	265^o	
30-70 H_2O, E.G.	-84^o	276^o	← Wow a Δ of $>350^o$

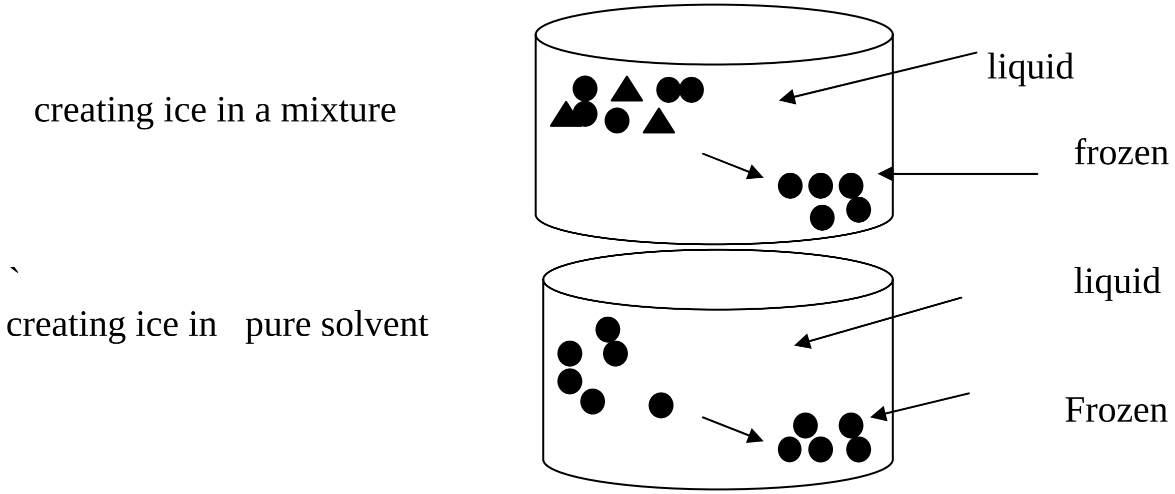
A three order of magnitude increase in temperature range!! A couple of points:

- That 50-50 mixture they tell you to use isn't as good as a 30-70 ratio—try impressing your Dad by telling him he can get an extra 50^oC of liquid range (especially useful in cold climates) by using a little less water.

- The incredible temperature range achieved isn't explained by anything I have mentioned but rather deal on interesting non-ideal effects that occur in mixtures, something you don't learn about unless you take upper division physical chemistry.

Colligative Property 2—freezing point depression is explained

Freezing point depression is again thermodynamic effect. In order to make ice, which is a pure crystal, extra work must be done to separate the ▲ solute from the ● solvent—NaCl from water, for example. This means you need to reduce the freezing point to thermodynamically drive the reaction. This has the advantage of allowing for the deicing of streets by requiring that a temperature lower than 0^{o}C be reached for ice to form. By the way, a lot of different kinds of compounds can be used to achieve this lower of the freezing point of ice. Salt is not the best candidate not only because it can cause only about a temperature drop of -15oC (making it useless when it gets colder) but also because it is so corrosive for automobiles. But it is cheap.



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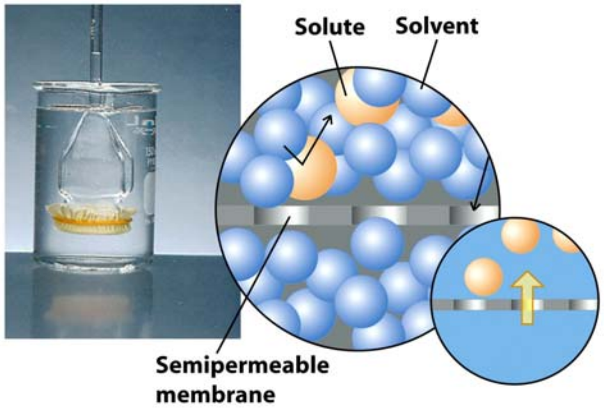
Colligative property 3: Osmotic pressure.

Osmotic pressure in action with good pictures.

The movement of solvent across a semi-permeable membrane to establish equal concentration. Note that whenever you give solutes a chance, they will distribute evenly across a solvent—for example, a few drops of food coloring to water and over time, a homogeneity of color results from equal concentration of the dye in the solvent.

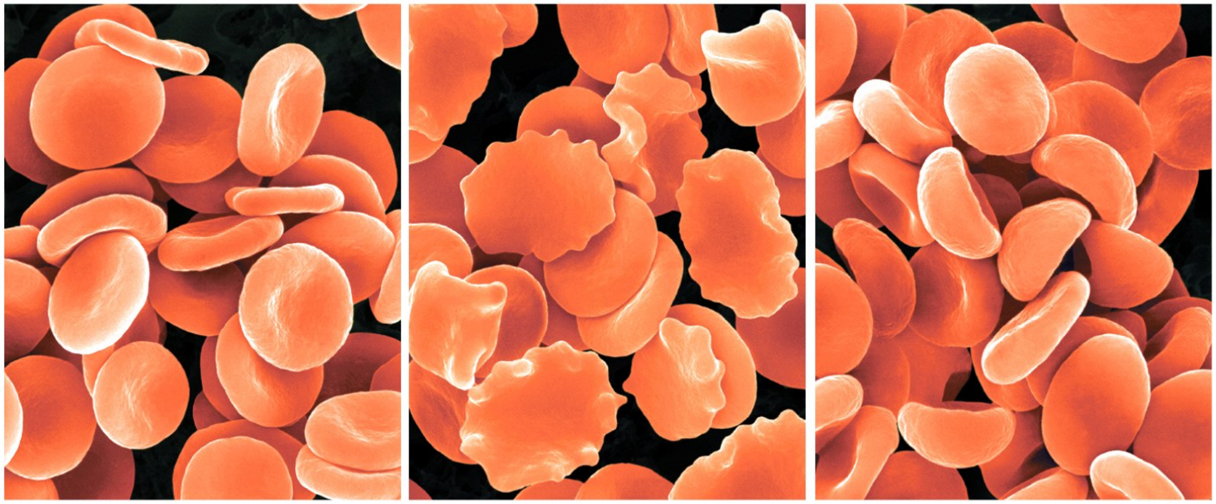
Now imagine that you create a barrier so that there is a selective ability to pass material throughout the solution. Semi-permeable membranes do this—they selectively allow one kind of molecule or another to cross the membrane. In the example shown, the membrane is cellulose acetate that selectively allows water to pass through to create the pressure differential.



Scientists are very creative at creating materials that allow one compound or another to selectively pass and so as you move along in science you will see many examples of selective mobility like this.

Of course the most famous example of a semipermeable membrane is the membrane in cells.   There is an elaborate process by which water and various electrolytes cross the cell membrane barrier—(I have tried to forget all this because I couldn’t get into medical school and no longer care about electrolyte imbalance. But all of you in Biology probably know this and could explain it to me if I cared.)

So in the picture of red blood cells below, note that just like the porridge in Goldilocks and the Three Bears, the solution around the cells be just the right concentration making for nice healthy cells (first picture), too high a concentration in which case the water flows out of the cell and they shrivel up (second picture), or too low a concentration in which case water flows into the cells and they lyse or rupture (third picture.)



Osmotic pressure in action with bad pictures..

In Figure A, note the concentration imbalance inside the baggie formed by the semi-permeable membrane. The concentration gradient that results drives ● selectively into the baggie across the membrane (the▲ cannot penetrate the baggie and leave. Consequently the large influx of ● to achieve a concentration balance results in an increase in pressure (osmotic pressure) inside the baggie.

Now imagine this happening in a cell, or heaven forbid, a fish. Your pet guppie, Toto, is happily swimming around in a dirty container of liquid in Figure C. Feeling badly for the fish and his dirty confines, you decide to place the fish in some clean water in Figure D. The water selectively enters the fish to ease the concentration gradient, and the increase in osmotic pressure, while a cleansing sort of thing in one respect, causes the fish to explode and die.

So now you know, it was you that killed your favorite pet.

Figure A—

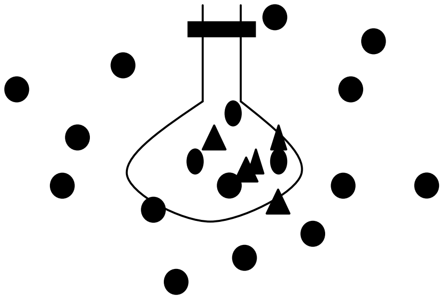


Figure B

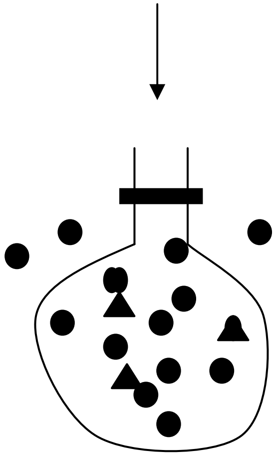


Figure C—dirty water

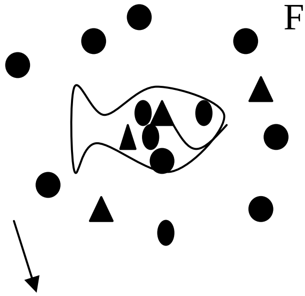


Figure D-clean water

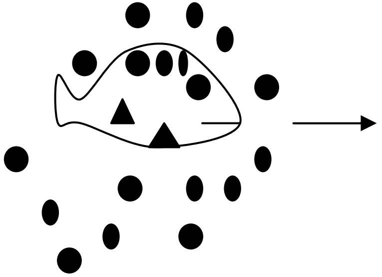


Figure E—R.I.P.