

Problem Set 9
Dill & Bromberg, chapter 16, problems 2, 7, 9, 12, 14, 16

16.2) Divers get the bends. We want to calculate the N₂ solubility in the blood as a function of depth in the water, and explain why the bends occur.

The relationship between the vapor pressure over a solution (or, the form of the nitrogen gas bubbles over its solution in the bloodstream) is given by Henry's law, $p=kx$, where k is the Henry's law constant for nitrogen gas in water.

The pressure of the air the diver is breathing D feet deep is $P = 1 + D/33\text{ft atm}$.

Nitrogen composes about 80% of the air, so its partial pressure is $0.80(1 + D/33)$ atm.

Therefore, the mole fraction of the solution which is nitrogen gas is:

$$x = \frac{p}{k} = \frac{0.80(1 + D/33\text{ft})\text{atm}}{86000\text{atm}}$$

Much more gas would dissolve in the diver's blood at the high pressures deep below the surface than at $p=1\text{atm}$ at the water's surface. Therefore, as the diver rises to the surface, the gas that dissolved deep underwater can no longer remain dissolved and bubbles out of his blood. This has nasty consequences for the diver. (ie, death, if not treated immediately)

16.7) Sparkling drinks. What mole fraction of CO₂ in water will lead to 'bubbling up' and a vapor pressure equal to 1atm?

The vapor pressure is again given by Henry's law: $p=kx$, so the mole fraction x :

$$x = \frac{p}{k} = \frac{760\text{mmHg}}{1.25 \times 10^6 \text{mmHg}} = 6.08 \times 10^{-4}$$

16.9) Oil/water partitioning of drugs. In partitioning a drug from oil into water, $\Delta s^0 = -50 \text{ cal (mol deg)}^{-1}$ and $\Delta h^0 = 0$ at $T = 300\text{K}$.

(a) What is $\Delta\mu^0$ at $T=300\text{K}$?

$$\Delta\mu^0 = \Delta h^0 - T\Delta s^0 = -(300\text{K})(-50 \text{ cal/molK}) = 15.0 \text{ kcal/mol}$$

(b) What is the partition coefficient from oil to water, K_{ow} , at $T=300\text{K}$?

$$\Delta\mu^0 = -RT\ln K_{ow}$$

$$K_{ow} = \exp\left(-\frac{\Delta\mu^0}{RT}\right) = \exp\left[-\frac{15\text{kcal/mol}}{(1.987\text{cal/molK})(300\text{K})}\right] = 1.18 \times 10^{-11}$$

(c) Assume that Δs and Δh are independent of temperature. Calculate K_{ow} at $T=320\text{K}$. (And, we must use $\Delta h^0 = 0$ as above.)

$$\Delta\mu^0 \text{ at } 320\text{K} = \Delta h^0 - T\Delta s^0$$

$$\Delta\mu^0 = -(320)(-50 \text{ cal/molK}) = 16.0 \text{ kcal/mol}$$

so,

Since $\Delta h^0 = 0$, K doesn't change with temperature, according to the van't Hoff equation.

16.12) Balancing osmotic pressures. A membrane-enclosed vesicle contains protein A that cannot exchange across the boundary, which causes osmotic flow of water into the

vesicle. The osmotic flow could be reversed by a sufficient concentration of a different nonexchangeable protein species B outside the membrane. The osmotic flow could be reversed because at low concentrations each distinguishable species of nonexchangeable component reduces the chemical potential independently of every other species.

16.14) Osmosis in plants. Plants must lift water from ground level to their leaves. Consider the roots as a capillary with radius 0.01cm whose walls are a semipermeable membrane with pure water on the outside and a solution inside with solute mole fraction $x = 0.001$. The solution inside has density 1 g cm⁻³. What is the height of the solution at room temperature?

For the ideal solution given, the osmotic pressure π across a membrane with chemical potential difference $\Delta\mu$ is given by:

$\Delta\mu = \pi v$ where v is the molar volume of the solute. (equation 16.31 in text)

And, from the equation on the bottom of page 292 (derived from equation 16.39), and from the free energy of transfer equation, 16.41, we know that:

$$\Delta\mu = kTx_{\text{solute}}$$

We need it in this form because we are given $x_{\text{solute}} = 0.001$.

Remember that $\Delta\mu$ is equivalent to energy, where the total energy = kinetic energy + potential energy. (This is just one of the many equations we know for energy, but this equation is relevant here because we need to know about the downward force on the water moving up.) At equilibrium, the water is no longer rising, so there is no kinetic energy, so the $\Delta\mu$ free energy equals the gravitational potential energy at equilibrium:

$$\Delta\mu = mgh.$$

We do not have the mass, but we can get mass from the volume and the density:

$$\Delta\mu = \rho Vgh$$

The volume of the cylinder is given by: $V = \pi r^2 h$ so,

$$\Delta\mu = \rho g \pi r^2 h^2.$$

Now we know all the parameters in these two $\Delta\mu$ equations so we can set them equal to each other:

$$\rho g \pi r^2 h^2 = kTx_{\text{solute}}$$

$$h^2 = \frac{kTx_{\text{solute}}}{\rho g \pi r^2} = \frac{(4.14 \times 10^{-14} \frac{\text{g} \cdot \text{cm}^3}{\text{s}^2})(0.001)}{(1 \frac{\text{g}}{\text{cm}^3})(980 \frac{\text{cm}}{\text{s}^2})(3.14)(10^{-4} \text{cm}^2)}$$

$$h \approx 10^{-8} \text{cm}$$

Therefore, although osmotic pressure does contribute to water transport inside of trees, other factors, such as transpiration of the water from the leaves, are much more important.

16.16) Ethane association in water. For the association of ethane molecules in water, $\Delta h^0 = 2.5 \text{ kcal mol}^{-1}$ at $T = 25^\circ\text{C}$. We want to know how the association constant K changes with temperature.

From the van't Hoff equation, $\ln K = -\frac{1}{RT}[\Delta h^0 - T\Delta s^0]$, we would be able to get a value for K if we knew Δs . Though we do not know Δs , we can still get an expression for the change of K with temperature (as long as we assume that Δh^0 and Δs^0 do not depend on T).

$$\ln K = -\frac{\Delta h^0}{RT} + \frac{\Delta s^0}{R}$$

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta h^0}{RT^2} = \frac{2500 \text{ cal/mol}}{(1.987 \text{ cal/molK})(298 \text{ K})^2} = 0.0142 \text{ K}^{-1}$$

As T increases, K increases, so the hydrophobic effect gets stronger.