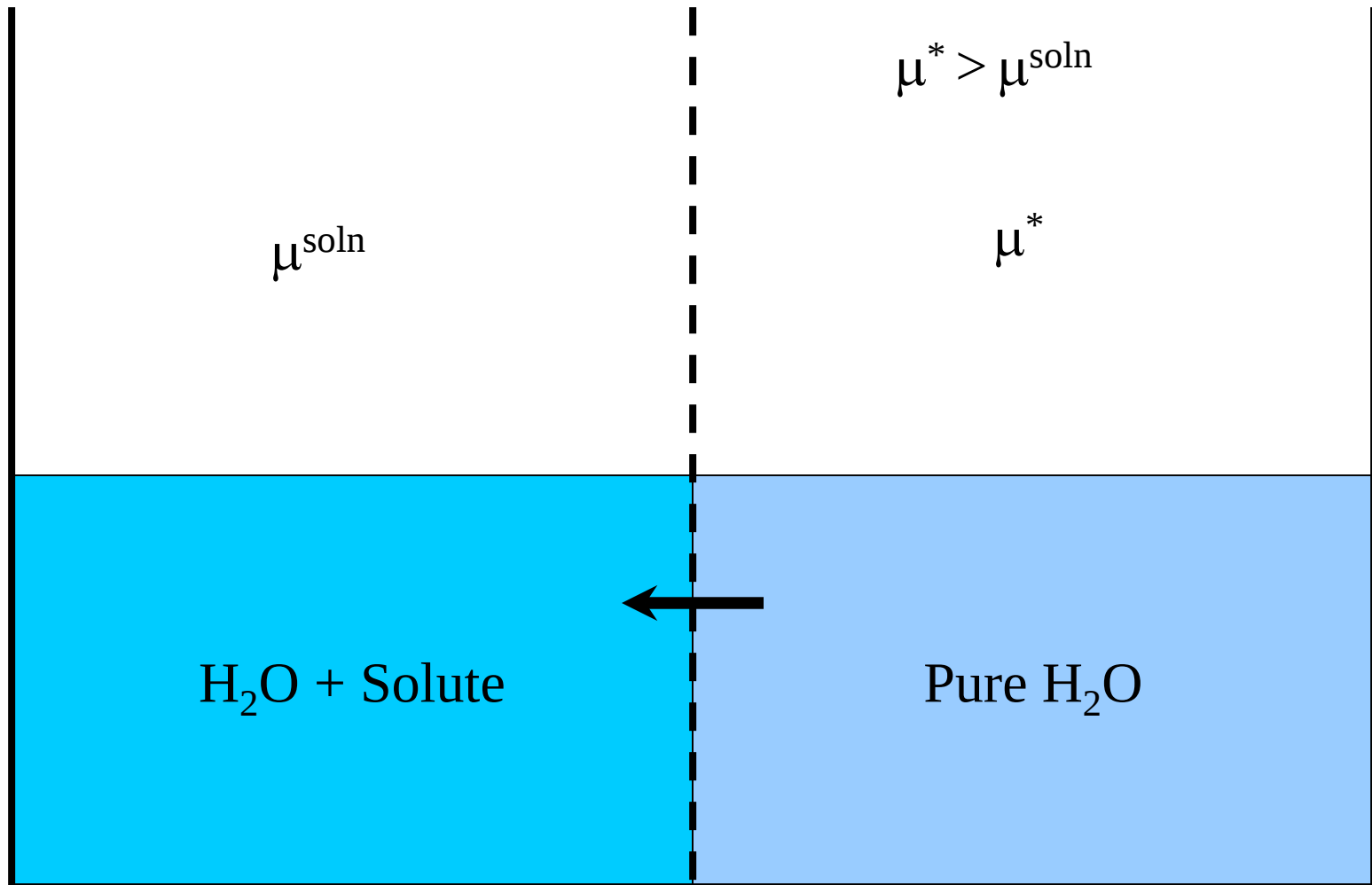


Osmotic pressure

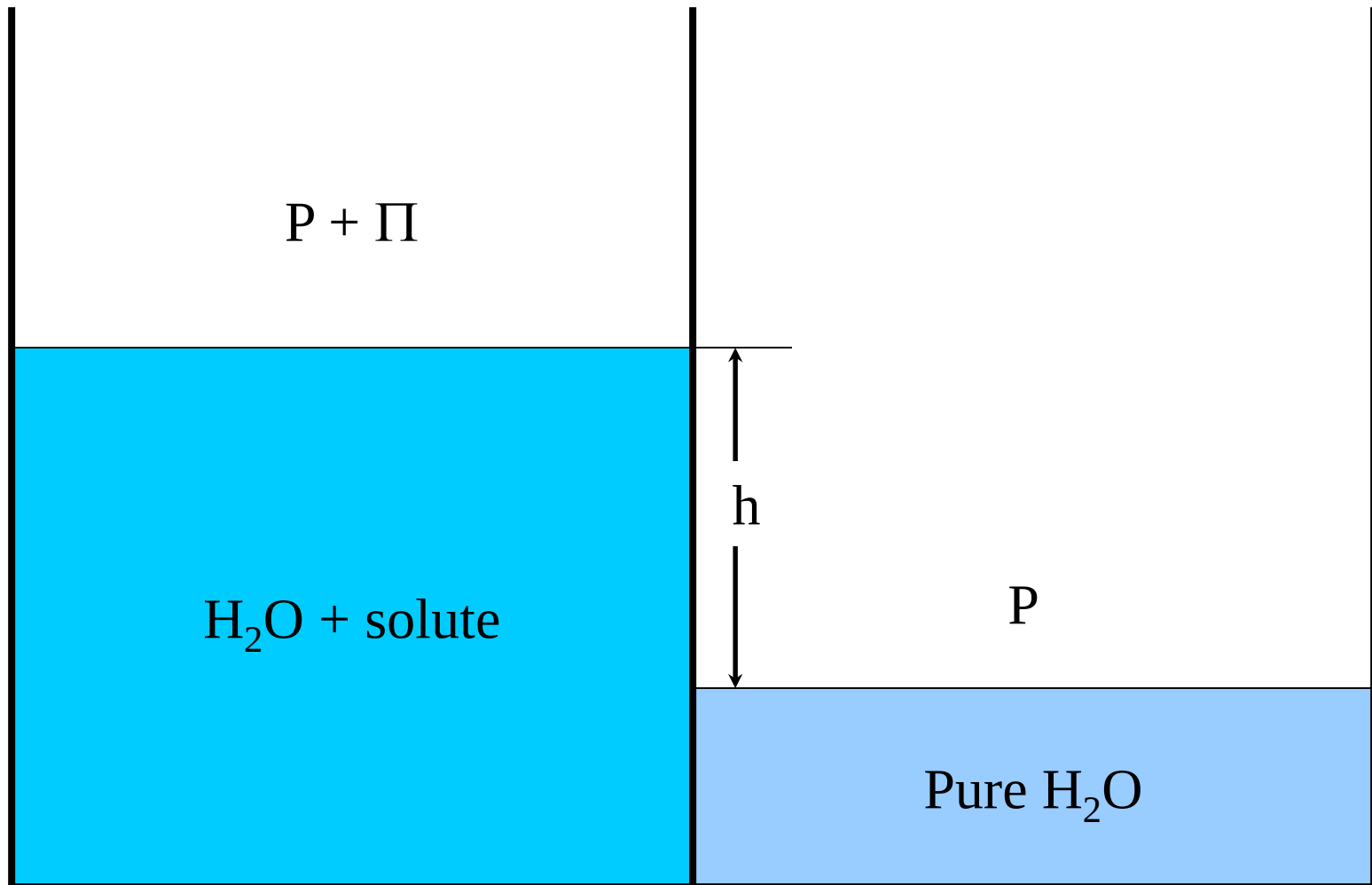
Osmotic pressure arises from requirement that the chemical potential of a pure liquid and its solution must be the same if they are in contact through a semi-permeable membrane.

Osmotic pressure is particularly applied to aqueous solutions where a semi-permeable membrane allows water to pass back and forth from pure water to the solution, but the solute cannot diffuse into the pure water. The point here is that the solute lowers the chemical potential on the solution side of the membrane and therefore there will be a tendency for water to move across the membrane to the solution side. Ultimately, there will be a balance of forces if a pressure builds up on the solution side of the membrane. This pressure can arise due to an increase in the hydrostatic pressure due to a rise in a column of solution or due to pressure inside a closed membrane. The easiest to visualize is a column of water.

Osmotic pressure arises from an imbalance in chemical potential when solute is added



The flow of solvent leads to an increase in hydrostatic pressure



Chemical potential moves toward equilibrium

Recall that the pressure at the bottom of a column of a fluid is given by $\Pi = \rho gh$. If water flows into the solution the height of the column of solution increases and the hydrostatic pressure also increases. At some point the chemical potential due to the concentration difference is exactly opposed to the chemical potential due to the pressure difference. We express this as

$$\mu_1^{soln}(T, P + \Pi, x_1) = \mu_1^*(T, P)$$

The chemical potential of the solution is

$$\mu_1^{soln}(T, P, x_1) = \mu_1^*(T, P) + RT \ln x_1$$

Here the equilibrium is shifted in terms of pressure (rather than temperature). We can break apart the considerations into two processes: 1. change in concentration, 2. change in pressure

Step 1: Osmotic pressure

The chemical potential has a dependence on pressure given by

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V_m$$

Therefore, the pressure dependent part can be written as

$$\mu_1^{soln}(T, P + \Pi) = \mu_1^{soln}(T, P) + \int_P^{P+\Pi} V_m dP$$

which gives simply

$$\mu_1^{soln}(T, P + \Pi) = \mu_1^{soln}(T, P) + \Pi V_m$$

and therefore,

$$\mu_1^{soln}(T, P + \Pi, x_1) = \mu_1^{soln}(T, P, x_1) + \Pi V_m$$

Step 2: Change in concentration

The mole fraction enters the chemical potential as

$$\mu_1^{soln}(T, P + \Pi, x_1) - \Pi V_m = \mu_1^*(T, P) + RT \ln x_1$$

which can be rearranged to

$$RT \ln x_1 + \Pi V_m = \mu_1^*(T, P) - \mu_1^{soln}(T, P + \Pi, x_1)$$

Since the chemical potentials are equal at equilibrium the right-hand side is zero.

$$\Pi V_m + RT \ln x_1 = 0$$

For a dilute solution and $\ln x_1 = \ln(1-x_2) \approx -x_2$ and therefore

$$\Pi V_m - RT x_2 = 0$$

Another van't Hoff equation!

The expression can now be written in the form.

$$\Pi V = n_2 RT$$

The above expression bears a surprising similarity to the ideal gas law. Keep in mind, however, that Π is the osmotic pressure and n_2 is the number of moles of solute. Thus, we can compute the osmotic pressure from

$$\Pi = \frac{n_2 RT}{V}$$

or

$$\Pi = cRT$$

where c is the molarity, n_2/V , of the solution. This equation is called the van't Hoff equation for osmotic pressure.

Use of osmotic pressure to determine molar mass

The van't Hoff equation can be modified to form used for the determination of molar mass by osmometry.

$$c = \frac{w}{M} \longrightarrow \Pi = cRT \longrightarrow \Pi = \frac{wRT}{M}$$

Here we related to the concentration c in moles/liter to the concentration w in grams/liter and the molar mass M in grams/mole.

The experimental configuration uses the measurement of height as an estimate of the osmotic pressure. The equation $\Pi = \rho gh$ is used ($h = \Pi/\rho g$).

Use of osmotic pressure to determine molar mass

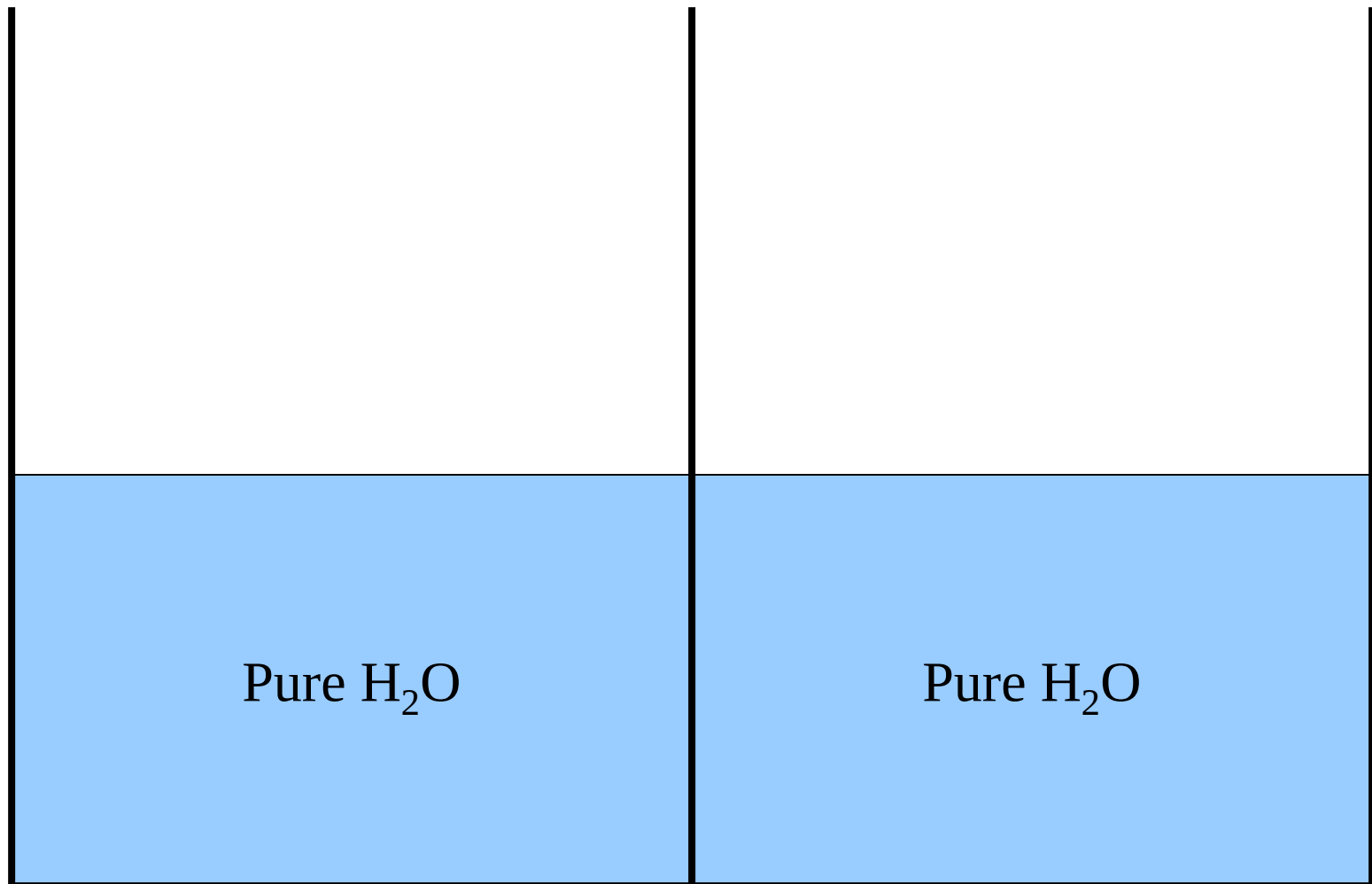
Vapor pressure osmometry uses a height measurement

$$h = \frac{wRT}{\rho g M}$$

to obtain the osmotic pressure and from that the molecular mass of a polymer (or biopolymer).

$$M = \frac{wRT}{\rho g h}$$

Use of osmotic pressure to determine molar mass



Use of osmotic pressure to determine molar mass

