

# STATISTICAL MOLECULAR THERMODYNAMICS

*Christopher J. Cramer*

Video 11.5

Other Colligative Properties

# BOILING POINT ELEVATION 1

Consider a gas in equilibrium with a solution where the liquid form of the gas is the solvent (e.g., steam in contact with an aqueous solution). In that case

$$\mu_1^{*\text{,gas}}(T_{\text{vap}}) = \mu_1^{\text{liq}}(T_{\text{vap}}) = \mu_1^{*\text{,liq}}(T_{\text{vap}}) + RT_{\text{vap}} \ln a_1$$

where  $T_{\text{vap}}$  is the temperature at which the gas and solution are in equilibrium.

Solving generally for  $\ln a$  as a function of  $T$  yields:

$$\ln a = \frac{\mu_1^{*\text{,gas}} - \mu_1^{*\text{,liq}}}{RT}$$

Now, differentiating with respect to  $T$

## BOILING POINT ELEVATION 2

$$\frac{\partial}{\partial T}(\ln a) = \frac{1}{R} \frac{\partial}{\partial T} \left( \frac{\mu_1^{*,\text{gas}}}{T} - \frac{\mu_1^{*,\text{liq}}}{T} \right)$$

Now, we can make use of the Gibbs-Helmholtz equation (cf. Video 8.7)

$$\left[ \frac{\partial(\mu/T)}{\partial T} \right]_{P, x_1} = -\frac{\bar{H}}{T^2}$$

to determine:

$$\frac{\partial}{\partial T}(\ln a) = \frac{1}{R} \left( \frac{\bar{H}_1^{*,\text{liq}} - \bar{H}_1^{*,\text{gas}}}{T^2} \right) = -\frac{\Delta_{\text{vap}} \bar{H}}{RT^2}$$

or, rearranging

$$d \ln a = -\frac{\Delta_{\text{vap}} \bar{H}}{RT^2} dT$$

*cf. freezing point depression*

# BOILING POINT ELEVATION 3

---

$$d \ln a = -\frac{\Delta_{\text{vap}} \bar{H}}{RT^2} dT$$

Integrating from the pure liquid ( $a = 1$ ,  $T_{\text{vap}} = T_{\text{vap}}^*$ ) to some other temperature corresponding to a particular solution (so  $a_1 < 1$ )

$$\int_{a=1}^{a=a_1} d \ln a = -\int_{T_{\text{vap}}^*}^{T_{\text{vap}}} \frac{\Delta_{\text{vap}} \bar{H}}{RT^2} dT$$

$$\ln a_1 = -\frac{\Delta_{\text{vap}} \bar{H}}{R} \left( \frac{1}{T_{\text{vap}}^*} - \frac{1}{T_{\text{vap}}} \right) \approx -\frac{\Delta_{\text{vap}} \bar{H}}{R(T_{\text{vap}}^*)^2} (T_{\text{vap}} - T_{\text{vap}}^*)$$

necessarily negative

necessarily positive

necessarily positive

i.e.,  $T_{\text{vap}} > T_{\text{vap}}^*$

Now define  $\Delta T_{\text{vap}} = T_{\text{vap}} - T_{\text{vap}}^*$

# SPECIFIC CASE OF WATER

$$\ln a_1 \approx -\frac{\Delta_{\text{vap}}\bar{H}}{R(T_{\text{vap}}^*)^2}\Delta T_{\text{vap}}$$

Now recall for the case of water (cf. Video 11.3):

$$\ln a_1 \approx \ln x_1 = \ln(1 - x_2) \approx -x_2 \approx -\frac{m}{55.51 \text{ mol kg}^{-1} \text{ water}}$$

and we finally have (for water)

$$\Delta T_{\text{fus}} \approx \frac{R(T_{\text{vap}}^*)^2}{\Delta_{\text{vap}}\bar{H} \cdot 55.51 \text{ mol kg}^{-1}} m$$
$$\approx K_b m$$

For water,  
 $K_f = 0.51 \text{ K kg mol}^{-1}$

*independent of solute!*

# Self-assessment

We'll soon see that some salts (strong electrolytes) separate into ions upon dissolution, so 1 mole of sodium chloride (table salt) added to a kg (~1 liter) of water would be 2 molal in ions.

Some sources suggest that one adds salt to pasta water in order to raise the boiling point so as to cook the pasta more effectively. For 1 lb of pasta, one might typically use about 1 gallon of water (~4 L, or 4 kg).

How much table salt (NaCl) would you need to add to a gallon of pasta water to raise the boiling point of the resulting brine solution by (a mere) 1 °C?

$$\Delta T_{\text{vap}} \approx \frac{R(T_{\text{vap}}^*)^2}{\Delta_{\text{vap}}\bar{H} \cdot 55.51 \text{ mol kg}^{-1}} m$$
$$\approx K_b m$$

# Self-assessment Explained

$$\Delta T_{\text{vap}} \approx \frac{R(T_{\text{vap}}^*)^2}{\Delta_{\text{vap}} \bar{H} \cdot 55.51 \text{ mol kg}^{-1}} m$$
$$\approx K_b m$$

For water,  
 $K_b = 0.51 \text{ K kg mol}^{-1}$

Given the value of  $K_b$  for water, it would appear that one will need about 1 mol of NaCl per 1 L (to make a 2 molal solution); so, that's 4 moles of NaCl for a gallon. With a molecular weight of 58.5 g/mol, that's 234 g, or about ½ pound (!) of NaCl in your pasta water.

Trust me. *Don't* try to raise your pasta water boiling point by that lousy 1 °C. Or, if you do, serve a lot of water with dinner...

# OSMOTIC PRESSURE

Recall:  $\left(\frac{\partial \mu_1^*}{\partial P}\right)_T = \bar{V}_1^*$

So,

$$\mu_1^*(T, P_{\text{atm}} + \Pi) - \mu_1^*(T, P_{\text{atm}}) + RT \ln a_1 = 0$$

$$\int_P^{P+\Pi} \left(\frac{\partial \mu_1^*}{\partial P'}\right)_T dP' + RT \ln a_1 = 0$$

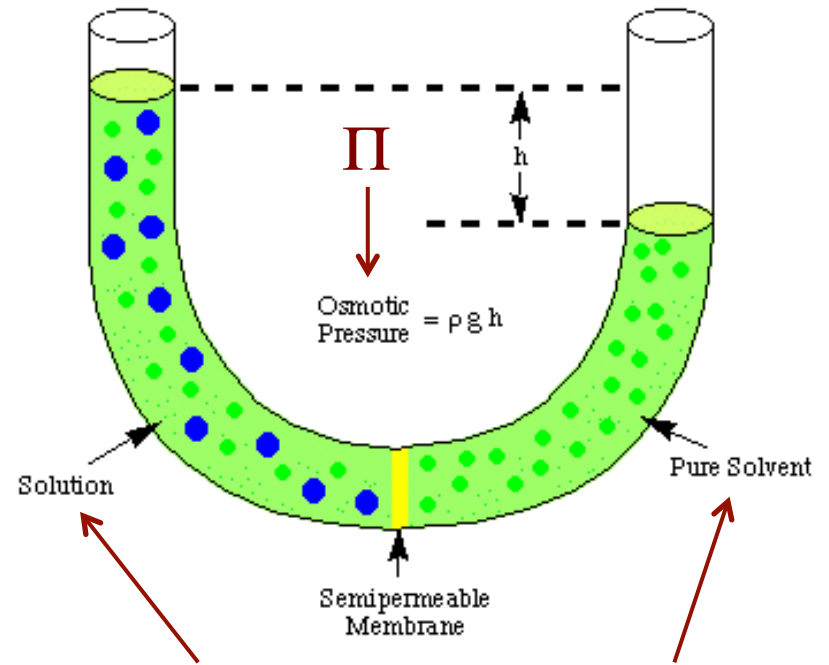
$$\mu_1^*(T, P_{\text{atm}} + \Pi) + RT \ln a_1 = \mu_1^*(T, P_{\text{atm}})$$

$$\Pi \bar{V}_1^* = -RT \ln a_1 \approx -RT \ln x_1 = -RT \ln(1 - x_2) \approx RT x_2 \approx RT n_2 / n_1$$

$$\Pi = cRT$$



*Useful for determining molecular weight of an unknown*



If osmotic pressure *exceeds*  $cRT$ , pure liquid will flow from the semipermeable membrane! For sea water, necessary pressure to desalinate the water is 26 atm at 15° C (column of water about 269 m high; or, about 87 stories...)



$$dU = \delta q + \delta w$$



*Next: Electrolyte Solutes*