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2.500 Desalination and Water Purification  
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## 2.500 DESALINATION AND WATER PURIFICATION

Homework Set #2  
Due 19 March 2009

### PROBLEM 1: TWO WAYS TO COMPUTE $\Pi$

We have seen that the osmotic pressure,  $\Pi$ , may be determined by considering the partial molar Gibbs energy of a solvent,  $i$ , as a function of pressure and composition at constant temperature,  $\bar{G}_i(p, x_i, T)$ . To further investigate this, consider a pure solvent at a pressure  $p^I$  and a solution having mole fraction of solvent  $x_i^{II}$  at a pressure  $p^{II}$ . At osmotic equilibrium,  $p^{II} - p^I = \Pi$ , the partial molar Gibbs energies are equal,  $\bar{G}_i(p^I, x_i^I, T) = \bar{G}_i(p^{II}, x_i^{II}, T)$ .

Calculate  $\Pi$  in two ways. First, assume a two step process going from (i) pure solvent at  $p^I$  to pure solvent at  $p^{II}$ , followed by (ii) change in composition from  $x_i^I = 1$  to  $x_i^{II}$  at fixed pressure  $p^{II}$ . Second, assume a two step process having (i) a change in composition from  $x_i^I = 1$  to  $x_i^{II}$  at fixed pressure  $p^I$ , followed by (ii) a change in pressure from  $p^I$  to  $p^{II}$  at fixed composition,  $x_i^{II}$ . Bear in mind that  $\bar{V}_i \equiv \partial \bar{G}_i / \partial p$ .

How do these two results differ? What do you conclude about the physical properties involved?

### PROBLEM 2: CONSTANT VOLUME MODEL FOR DENSITY OF SALT WATER

To estimate the density of salt water (aqueous NaCl), we could try assuming that the volume of solution remains fixed when salt is added to water, so that salt water containing 1 kg of H<sub>2</sub>O would have the same volume as 1 kg of pure water. Calculate the density of salt water as a function of molality on this basis and compare it to the data given in the paper by Pitzer et al. on the Stellar site (see pg. 84) at 25°C. Also give the mass fraction of NaCl for each case. How well does this model compare with the data?

### PROBLEM 3: OSMOTIC COEFFICIENT FOR SEPARATION CALCULATIONS

The osmotic coefficient,  $\phi$ , is related to the chemical activity as

$$\ln a_w \equiv -\phi M_w (10^{-3} \text{ kg/g}) \left( \sum_i m_i \right)$$

where  $M_w$  is the molar mass of the solvent in grams/mol and  $\sum_i m_i$  is the sum of the molalities of all solutes. Determine whether changes in the partial molar Gibbs energy of salt water (e.g., as in the examples done in class or in Homework 1) can be calculated with less error by using the osmotic coefficient than by using the activity coefficient and mole fraction of water. Do this by considering the removal of a small amount of fresh water from a large volume of  $m_{\text{NaCl}} = 0.62$  mol NaCl/kg H<sub>2</sub>O solution at 25°C and looking at the impact on the answer of a 0.5% change in either  $a_w$  or  $\phi$ .

#### PROBLEM 4: IONIC ACTIVITY COEFFICIENTS FROM OSMOTIC COEFFICIENTS

It may be shown that\*:

$$\ln \gamma_{\pm} = -2 \int_0^{m^{1/2}} \frac{(1 - \phi)}{m^{1/2}} d(m^{1/2}) - (1 - \phi)$$

in which  $\phi$  is the osmotic coefficient of the solvent and  $\gamma_{\pm}$  is the mean ionic activity coefficient of the solute. This equation was traditionally solved graphically, by plotting  $(1 - \phi)/m^{1/2}$  versus  $m^{1/2}$  and finding the area under the curve.

For the following osmotic coefficients of aqueous potassium chloride solution at 25°C, calculate the mean ionic activity coefficient at various molalities.

$m$	$\phi$	$m$	$\phi$
0.1	0.926	0.7	0.898
0.2	0.913	1.0	0.899
0.3	0.906	1.5	0.906
0.5	0.900		

#### PROBLEM 5: CROSS-FLOW SEPARATOR LIMITING EQUATION

In class, we derived an equation for the average permeate concentration,  $\bar{c}_{s,p}$ , in a crossflow separator. Show that for small values of the salt passage, SP, this equation can be written as

$$\bar{c}_{s,p} = -SP \left( \frac{\ln(1 - R_p)}{R_p} \right) c_{s,f}$$

#### PROBLEM 6: FORWARD OSMOSIS

Recently, it has been proposed that *forward osmosis* can be used to separate water from seawater. The concept is to use a concentrated “carrier solution” having higher osmotic pressure than seawater to draw water from seawater into the concentrate through a membrane. In other words, water flows into the carrier solution to dilute it, without the applied pressure used in reverse osmosis. Following this, water is extracted from the carrier solution. For example, the carrier solution might contain absorbed gases that can easily be desorbed later, leaving pure water behind.

Investigate methods of separating water from the carrier solution (and the associated choice of a carrier solution), and comment on the overall advantages of this process. Is forward osmosis energetically more efficient than reverse osmosis, or will the purification of the carrier water include a corresponding energy penalty? (You may consult the research literature as desired to learn more about this process. See, for example, the paper by Cath et al. on the Stellar site.)

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\*This is a consequence of the Gibbs-Duhem equation. See, e.g., S. Glasstone, *Thermodynamics for Chemists*. New York: Van Nostrand Co., 1947, §§38f, 39f, 39g. (Available in Google Books). For a 1-1 electrolyte such as KCl, the argument of the integral tends to 0.391 as  $m \rightarrow 0$  (see eqn. 41.8 in Glasstone).

## PROBLEM 7: SIZE AND ENERGY CONSUMPTION OF AN RO SYSTEM

A single-stage seawater reverse osmosis system is being designed for use with 35,000 ppm seawater at 20°C. An output of 10,000 m<sup>3</sup>/day is desired at a product recovery  $R_p$  of 50%. Product water should have TDS below 250 ppm. The system uses spiral-wound modules (type SWC5, data given below). There are eight modules per pressure vessel, with an array of pressure vessels working in parallel. The system can be modelled as a one-pass crossflow separator using the equations discussed in class.

In addition to the high pressure pump, a power recovery turbine is included. The turbine may be assumed to be coupled directly to the pump shaft, thus lowering the electrical work required from the pump motor.

Various additional data are given below.

Determine the required membrane area, the number of pressure vessels, and the net power consumption of this system in kW. Also find: the net power in kJ per kilogram of fresh water produced, the salt concentration of the permeate and the salt concentration of the concentrate (or retentate).

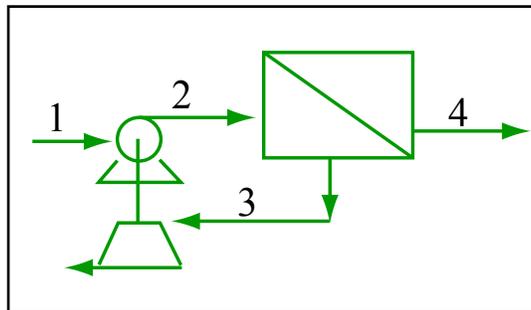


Figure by MIT OpenCourseWare.

## Design Data for Reverse Osmosis System

seawater pressure after pump	$p_2 = 61 \text{ bar}$
outlet concentrate pressure	$p_3 = 59.7 \text{ bar}$
permeate and supply pressures	$p_4 = p_1 = 1 \text{ bar}$
feed concentration	$c_{s,f} = 35000 \text{ ppm NaCl}$
permeate flow rate	$\dot{V}_p = 10000 \text{ m}^3/\text{day}$
product recovery ratio	$R_p = 0.50$
pump efficiency	$\eta_p = 0.86$
turbine efficiency	$\eta_t = 0.86$
pump motor's efficiency	$\eta_m = 0.94$
membrane area per module	$A_m = 36.8 \text{ m}^2$
membrane permeability	$A = 1.3 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar at } 25^\circ\text{C}$
salt rejection	$\text{SR} = 99.8\% \text{ at membrane test flux of } 34 \text{ L/m}^2 \cdot \text{h}$

### Notes.

- A. To evaluate the driving pressure difference, take the average of the inlet and outlet conditions, and treat it as constant over the flow path.
- B. You may ignore concentration polarization effects in this problem.
- C. You should not ignore the effect of temperature.
- D. The density of the brine varies with salinity; however, our model equations do not account for this effect. It may be neglected to within an error of a few percent in concentration.
- E. The salt rejection varies with the water flux through the membrane. To adjust the salt rejection to the value for this system's average water flux, the salt passage,  $\text{SP} = 1 - \text{SR}$ , is used. Specifically,  $\text{SP} \times \text{water flux} = (c_{s,\text{permeate}}/c_{s,\text{feed}}) \cdot J_v = J_s/c_{s,\text{feed}} \approx B = \text{solute permeability coefficient (constant at constant temperature)}$ . In other words,

$$\text{SP} \times J_v = \text{constant for given temperature.}$$

The main effect of changing the salt rejection will be on  $\bar{c}_{s,p}$ . Thus, the calculations may be done using the nominal salt rejection given above to find the membrane flux, and then corrected to the proper SR before taking a final value of  $\bar{c}_{s,p}$ .