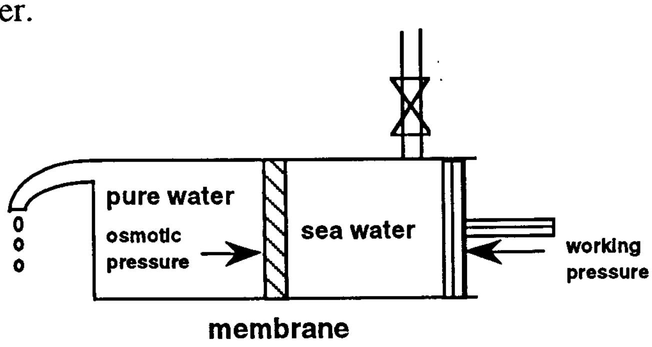
88 年度博士資格考試

化工熱力学

Part I.

(1). In a seawater desalination system, a semi-permeable membrane is applied to purify water from seawater. For a reversible process, a working pressure equal to the osmotic pressure (π) is necessary to apply on the seawater side so as to obtain pure water.



Question 1: Explain why the working pressure is just the osmotic pressure for a reversible process? Please also explain for what reason that the working pressure must be much larger than the osmotic pressure for a real process?

Question 2: What is the minimum pressure to desalinate seawater, assumed to be 3.5 wt.% NaCl (molar fraction 0.0214)? (please use ideal solution assumption

(a) Write down the chemical potential (Gibbs free energy) for the solution?

(b) Applying that $(\partial\mu/\partial P)_T = V$, μ = chemical potential, find the difference of the solvent chemical potential in the mixed state and in the pure state? Please express it as a function of pressure and volume?

(c) Using the final equation $\ln(1-x) = -V_{water}(P_1 - P_0)/RT$, where x is the molar fraction of solute, V of water at 298K is 18 cc/mol, R is 83.14 cc bar/mol K, $(P_1 - P_0)$ is the osmotic pressure? (25%)

(2). Determine whether the following process violates the laws of thermodynamics. An ideal gas of constant heat capacity (C_p = 30 kj/kmol K) at 10 bar and 295 K enters a device which is thermally and mechanically insulated from the surroundings. One-half of the gas leaves the device at 355 K and 1 bar, while the other half leaves at 235 K and 1 bar. (25%)

Part II.

1. A gaseous mixture contains 40 mol % A and 60 mol % B. The mixture is cooled down to 200 K through a Joule-Thomson expansion and then sent to a distillation column operating at 1 bar. If the temperature of upstream of the throttling valve is 300 K, what is the required upstream pressure? The volumetric properties of this gaseous mixtures are given by

$$\underline{V} = \frac{RT}{P} + 100 - \frac{10^5}{T}$$

where $\underline{V}$ is the molar volume (cm^3/mol) and R = 83.1439 bar cm^3/(mol K) = 8.31439 J/(mol K). The heat capacities at ideal gas state (C_p^o) are 30 J/(mol.K) for A and 40 J/(mol.K) for B. Other thermodynamic relationships: $d\underline{H} = T\, d\underline{S} + \underline{V}\, dP$, and $d\underline{S} = \frac{C_P}{T} dT - \left(\frac{\partial \underline{V}}{\partial T}\right)_P dP$. (20%)

2. A volumetric equation of state is generally expressed as $P = f(T, \underline{V})$, such as the Peng-Robinson (PR) equation. The PR equation was defined as

$$P = \frac{RT}{\underline{V} - b} - \frac{a(T)}{\underline{V}(\underline{V} + b) + b(\underline{V} - b)} \quad (4\text{-}1)$$

$$a(T) = a(T_c) \times \alpha(T) = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha(T) \quad (4\text{-}2)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (4\text{-}3)$$

$$\alpha(T) = [1 + \kappa(1 - \sqrt{T/T_c})]^2 \quad (4\text{-}4)$$

with

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (4\text{-}5)$$

where ω is the acentric factor and the subscirpt "c" refers to critical property.

(a) Why the PR equation is categorized as a cubic type equation of state? (2%)

(b) What the properties are needed to be known for each fluid in the calculation with the PR equation? (3%)

(c) Discuss how to obtain eqs. (4-2) and (4-3). (You don't need to derive them) (3%)

(d) Although $\alpha(T)$ is defined empirically as usual, it should satisfy a certain of necessary condition. Please give this condition. (2%)

(e) Discuss how to obtain eq. (4-5). (5%)

3. The UNIFAC activity coefficient model was developed on the basis of group-contribution approach. Briefly describe its advantages and limitations for engineering applications. (15%)