九十學年度資格考

化工熱力學

1. The rain was scare until April of this year. It seems that making pure water from seawater is a way for emergency usage in a drought. Figure 1 is a schematic of producing pure water from seawater by distillation. The seawater (mole ratio of ions x_s = 0.02) at 100 ℃ is flowing into a tank which is evacuated down to 0.98 atm. Under this condition, the seawater boils and the vapor is compressed up to 1 atm so as to condense to pure water.

Question 1: Considering that seawater obeys ideal solution behavior, please write down the relation between the vapor pressure of pure water (P_0) and the vapor pressure of water in seawater (P).

Question 2: If the pumping is a reversible isothermal compression process, write down the work necessary for pumping 1 mol of water vapor from P to P_0. Also express the work done (w) as a function of x (using the relation: $\ln(1-x) = -x$, when x is far less than 1).

Question 3: Reverse osmosis is also a technique to desalinate seawater which applies a semipermeable membrane letting water molecules pass through but the ions not (Fig. 2). Considering that this process also operates in a reversible manner, i.e., the pressure exerted at the seawater side is just the osmotic pressure of the seawater system (π), please start from (i) ideal solution equation: $\overline{\mu} = \mu_i + RT\ln x_i$ (where $\overline{\mu}$ is the component chemical potential, μ_i is the chemical potential in pure state, and x_i is the mole ratio of the component) and (ii) $du = -SdT + VdP$:

(a) Please derive osmotic pressure of seawater (π) as a function of the mole ratio of ions (x_s) in the seawater.

(b) Show that the work (w) necessary for producing 1 mol pure water by reverse osmosis technique is $w = x_s RT$ (R is the ideal gas constant and T is the temperature). Please also compare this result with the outcome in question 2 and explain why. (30%)

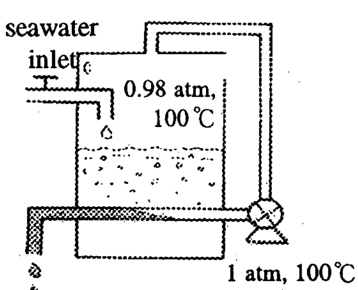

Fig. 1 distillation method

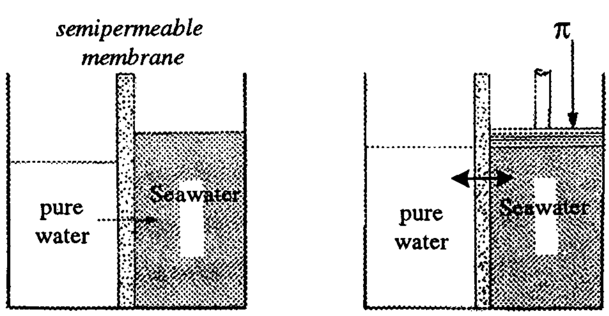

Fig. 2 osmotic pressure of the seawater system

2. Aqueous emulsions of perfluorochemicals are being considered as "artificial bloods" because of their high oxygen solubility. At 25℃ and an oxygen pressure of 1 atm, 384 ml of oxygen gas (measured at 25 ℃ and 1 atm) dissolve in 1 liter of perfluorotributylamine, $(C_4F_9)_3N$, which has a liquid density of 1.883 g/ml.

Question 1: Determine the Henry's law constant, in units of atmospheres, for oxygen dissolved in perfluorotributylamine. The corresponding value for oxygen dissolved in water is 4.38×10^4 atm.

Question 2: The blood substitute *Oxypherol* is an emulsion of 20% perfluorotributylamine and 80% water by volume. Estimate the volume of oxygen gas (measured at 25℃ and 1 atm) dissolved in a liter of liquid *when Oxypherol* is equilibrated with air at 25℃. (20%)

3. The virial equation gives the compressibility factor for gases as a power series as:

$$Z = \frac{pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \cdots \quad (1)$$

where B is the second virial coefficient, C is the third virial coefficient, D is the fourth, and so on. The first term on the right is unity, and by itself provides the ideal-gas value for Z. The remaining term provide corrections to the ideal-gas value, and of these the second term $\frac{B}{v}$ is the most important. Statistical mechanics provides B for simple, spherically symmetric molecules as

$$B = 2\pi N_A \int_0^\infty (1 - e^{-\Gamma(r)/kt}) r^2 dr \qquad (2)$$

where N_A is Avogadro's number, $\Gamma(r)$ is the potential function.

Question 1: State briefly an experimental method to determine the second virial coefficient B.

Question 2: Second virial coefficient can be corrected to the potential function only if the form of the potential function is known. Lennard-Jones' form of Mie's potential is the most widely used and is given as

$$\Gamma(r) = 4\varepsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6], \qquad (3)$$

where ε is the depth of the energy well, σ is the collision diameter, and r is the distance. Please draw a graph to show the meaning of each term in eq. (3).

Question 3: Usually, evaluating second virial coefficient B from Lennard-Jones' potential requires numerical technique. Instead, a crude potential named the "square-well potential" which has the general shape of the Lennard-Jones function, can be used to make mathematics easier. The square–well potential function is

$$\Gamma = \begin{cases} \infty & \text{for } r \le \sigma \\ -\varepsilon & \text{for } \sigma < r \le l\sigma \\ 0 & \text{for } r \ge l\sigma \end{cases}$$
,

where l is the reduced well width. The square-well potential leads to

$$B = \frac{2}{3}\pi N_A \sigma^3 [1 - (l^3 - 1)(e^{\frac{\varepsilon}{kT}} - 1)]$$

From the above result, explain the meaning of the first term in the square brackets (i.e., 1) and the second term. Also explain why B is usually negative at low temperature and turns to positive at high temperature. (30%)

(4) The energy E in a canonical ensemble, which in classical thermodynamics is the internal energy U, is given by $U = E = \sum_i p_i^* E_i$, where p_i^* is the probability that a given system of the canonical ensemble is in quantum state i with the energy eigenvalue E_i. Note that $p_i^* = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$ (where β is a mechanical parameter as $\beta = \frac{1}{kT}$, k is the Boltzmann constant and T is the temperature) and $dE_i = (\frac{\partial E_i}{\partial V})_N dV$ (N is the number of molecules, V is the volume).

Question 1: Start from the differentiation of dE_i and compare it with the classical thermodynamics $dU = TdS - PdV$ to show the statistical analogue for the entropy S to be $S = -k\sum_i p_i^* \ln p_i^*$.

Question 2: Under what condition does the entropy S turn to the so-called the Boltzmann relation $S = k \ln W$ (W is the thermodynamic probability) ? (20%)