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 $x_i = 0.02$) at 100 °C 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 ($\pi$), please start from (i) ideal solution equation: $\overline{\mu} = \mu_i + RT \ln x_i$ (where $\overline{\mu}$ is the component chemical potential, $\mu_i$ 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 ($\pi$) as a function of the mole ratio of ions ($x_i$) in the seawater.

(b) Show that the work ($w$) necessary for producing 1 mol pure water by reverse osmosis technique is $w = x_i RT$ ($R$ 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](image1)

![Fig. 2 osmotic pressure of the seawater system](image2)
2. Aqueous emulsions of perfluorochemicals are being considered as “artificial bloods” because of their high oxygen solubility. At 25°C and an oxygen pressure of 1 atm, 384 ml of oxygen gas (measured at 25°C and 1 atm) dissolve in 1 liter of perfluorotributylamine, (C₆F₁₃)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 × 10⁴ 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°C and 1 atm) dissolved in a liter of liquid when *Oxypherol* is equilibrated with air at 25°C. (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 \( B/V \) is the most important. Statistical mechanics provides \( B \) for simple, spherically symmetric molecules as

\[
B = 2\pi N_A \int_0^\infty (1 - e^{-\Gamma(r)/kT}) r^2 dr \quad (2)
\]

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

\[
\Gamma(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6], \quad (3)
\]

where \( \varepsilon \) is the depth of the energy well, \( \sigma \) 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
\[ \Gamma = \begin{cases} \infty & \text{for } r \leq \sigma \\ -\varepsilon & \text{for } \sigma < r \leq l\sigma \\ 0 & \text{for } r \geq l\sigma \end{cases} \]

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

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

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. \( \text{(30\%)} \)

\textbf{(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 \( \beta \) is a mechanical parameter as \( \beta = \frac{1}{kT} \), \( k \) is the Boltzmann constant and \( T \) is the temperature) and \( dE_i = (\frac{\partial E_i}{\partial V})_N dV \) \((N \text{ is the number of molecules, } V \text{ is the volume})\).

\textbf{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

\[ S = -k \sum_i p_i^* \ln p_i^* . \]

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