

Sheet 10

Please hand in your solutions before the Wednesday lecture on Jan 21 at 10:15.

Problem 1 : Osmotic pressure (20 points)

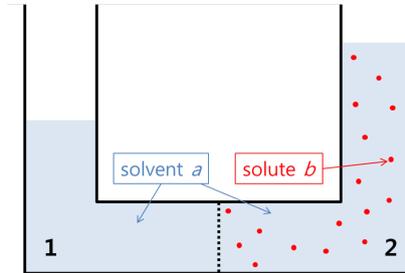


Fig. 1: A container of solvent (blue, a) and solute (red, b) particles partitioned by a semi-permeable membrane (broken line) through which only the solvent particles can pass.

As depicted in Fig. 1, consider a tube with a semi-permeable membrane. The membrane allows only the solvent particles to pass through it, such that in the left-hand side of the tube (“1”) there only exist solvent particles, while in the right-hand side (“2”, volume V) there exists a mixture of N_a solvent particles and N_b solute particles. The mixture is dilute such that N_b is much smaller than $N = N_a + N_b$, hence the solute particles are assumed to be non-interacting.

- (5 points) Denoting the entropy of the solvent particles in the right-hand side by S_a , find the entropy of the mixture S_{mix} , and using S_{mix} calculate the osmotic pressure $p_{osm} = p_{mix} - p_a$, where p_{mix} is the pressure of the mixture and p_a is the pressure of the solvent particles.
- (5 points) The chemical potential μ_1^a of the solvent particles in the left-hand side is equal to the chemical potential μ_2^a in the right-hand side. Using this, calculate the osmotic pressure $p_{osm} = p_{mix} - p_a$.
- (10 points) Consider a cell in which there are biological macromolecules with a number fraction $1/200$ with respect to the water molecules, i.e. there is one macromolecule per 200 water molecules in the cell, so it is dilute solution. One mole of water molecules has a volume $\approx 20 \text{ cm}^3$. Calculate (give a numeric value) the osmotic pressure of the cell in units of atm at 300 K.

Problem 2 : Change in boiling temperature and melting temperature (10 points)

Consider a **DILUTE** solution which includes N_a^l solvent particles and N_b solute particles, at temperature T , pressure p , and volume V . There also exists gas phase of N_a^g vaporized solvent particles, where p_0 is the vapour pressure of the pure solvent at temperature T .

- (2 points) What is the vapour pressure? Express it in one sentence.
- (3 points) Due to the solute particles, the vapour pressure p_v of the solution will be lowered from p_0 . Calculate $p_v - p_0$.
- (5 points) Show that, as a consequence of the lowered vapour pressure, the solution has for the same pressure a higher boiling point $T^{boil} > T_0^{boil}$ and a lower melting point $T^{melt} < T_0^{melt}$ than the pure solvent.

Problem 3 : Diamond-graphite phase transition (10 points)

Due to the different crystal structures, the Gibbs free energy G of one mole of diamond (volume $3.0 \times 10^{-6} \text{ m}^3$) is 2.9 kJ greater than that of one mole of graphite (volume $5.0 \times 10^{-6} \text{ m}^3$), at 300 K and 1 bar. One mole of diamond can be converted to graphite, with entropy increased by 3.4 J/K, and volume increased by $2.0 \times 10^{-6} \text{ m}^3$, at 300 K.

- (5 points) Sketch a plot of G (kJ) as function of pressure p (kbar), at 300 K. Estimate the minimal pressure for diamond to get stable than graphite.
- (5 points) Sketch a phase diagram of p (kbar) - temperature T (K).

Problem 4 : Low density gas (10 points)

For a low-density gas the virial expansion can be terminated at first order in the density and the equation of state is:

$$P = \frac{Nk_B T}{V} \left[1 + \frac{N}{V} B_2(T) \right] \quad (1)$$

where $B_2(T)$ is the second virial coefficient. The heat capacity will have corrections to its ideal gas value. We can write it in the form

$$C_{V,N} = \frac{3}{2} Nk_B - \frac{N^2 k_B}{V} f(T) \quad (2)$$

- (3 points) Find the form that $f(T)$ must have in order for the two equations to be thermodynamically consistent.
- (4 points) Find the entropy and internal energy as partial derivatives of the Helmholtz free energy, A (*Hint*: $P = -\left(\frac{\partial A}{\partial V}\right)_T$).
- (3 points) Find $C_{P,N}$.

Remark: The virial expansion is the most interesting and versatile of the equations of state for gases. The virial expansion is a power series in powers of the variable, N/V , and has the form

$$\frac{PV}{Nk_B T} = 1 + \frac{N}{V} B(T) + \frac{N^2}{V^2} C(T) + \dots \quad (3)$$

The coefficient, $B(T)$, is a function of temperature and is called the second virial coefficient. $C(T)$ is called the third virial coefficient, and so on.

Problem 5 : Van der Waals-like gas (Bonus task, 10 points)

For an ideal gas the single partition function is $z_1 = V/\lambda^3$, where $\lambda = \sqrt{h^2/(2\pi m k_B T)}$ is the thermal wavelength. If the gas has the minimum volume v occupied by a particle and interaction energy U , z_1 can be approximately modified as

$$z_1 = \frac{V}{\lambda^3} \Rightarrow \frac{V - Nv}{\lambda^3} e^{-N\langle U \rangle / k_B T}, \quad (4)$$

where $\langle U \rangle$ is average of the interaction energy $U(r)$ over radial distance r between particles (the volume integral).

- (2 points) What is the physical meaning of the exponential term in the above modification Eq. (4)?
- (2 points) Show that the equation of state of this gas is $\left(p + N^2 \frac{d\langle U \rangle}{dV}\right) (V - Nv) = Nk_B T$.
- (3 points) The critical point is obtained where both the first and second derivatives of p with respect to V are zero. Show that at critical point $V_c = 3Nv$, $T_c = \frac{8V^2}{27k_B v} \frac{d\langle U \rangle}{dV}$, and $p_c = \frac{V^2}{27v^2} \frac{d\langle U \rangle}{dV}$.
- (3 points) Consider the screened Coulomb potential $U(r) = -(\alpha k_B T e^{-r/\sigma}) / (8\pi r)$ for $\sigma < r < \infty$, where α is a certain length scale. Calculate $\frac{d\langle U \rangle}{dV}$ and express the the equation of state.