

Assignment 4: CHM221A  
Topic: Thermodynamic stability/ Phase  
transition

Mainak Sadhukhan

October 16, 2023

**To students:** These assignments are designed to strengthen your understanding in the lessons taught in class as well as develop your problem solving skills. If you copy from other sources without understanding, those purposes will be defeated and you will receive no benefits. **If you cannot solve them, try and bring your problems to the instructor. He will definitely help. Also, there may be some typo - discuss with me if you think there are any.**

1. The sublimation enthalpy  $h_{sub}$  (Latent heat for solid to gas transition) for a substance X is measured to be 62.4 kJ/mol at 273.15 K, kept at  $10^5$  Pa pressure in a closed container. Considering the  $h_{sub}$  does not change with temperature and pressure, calculate the vapour pressure of the gas inside the container at 300 K.
2. Two moles of a substance is kept inside a container of 10 cc. Its liquid form of molar volume 1 cc/mol is coexisting with its vapour of molar volume 20 cc/mol. What is the mole fraction of the vapour phase?
3. Find the critical temperature  $T_{cr}$  and critical pressure  $P_{cr}$  of a van der Waals gas.

**Hint: See Callen, Chapter 9, worked out examples**

4. The vapour pressure (in Pa) of a substance in liquid phase behave as

$$\ln(P) = 50.31 - \frac{1000}{T}$$

while the vapour pressure of solid phase behaves as

$$\ln(P) = 82.92 - \frac{5000}{T}$$

Find out the triple point of the system.

**Hint: At triple point, the liq-gas and solid-gas line intersect. See Callen, Problem 9.3-5**

5. If I ever come to the class and declare that in the last night I discovered three Ice phases (solid water) A, B and C can coexist with liquid water at  $-23^\circ\text{C}$  and 1 atm pressure, how will you refute my claim and force me to read my own lecture notes?
6. Prove that for a binary alloy, the Eutectic temperature is a smooth function of pressure (i.e.  $T_E \equiv T_E(P)$ ).
7. Two volatile liquids A and B are mixed in a closed container. The condensation curve for A is given by (Temperature in K and  $x_A$  is the mole fraction of A)

$$T_{cond} = 20 - 5x_A^2$$

while its boiling curve is given by

$$T_{boil} = 20 - (x_A + 4x_A^2)$$

at 1 atm pressure.

- (a) Find out the boiling point of pure components.
- (b) The 3 : 2 gas mixture of temperature 100 K is cooled down to 18.5 K. What should be the composition of the vapour now.
- (c) Suppose, successively ( $n = 0, 1, 2, \dots$ ) we are reducing the temperature of the mixture according to

$$T_{n+1} = T_n - n \frac{T_0}{10}$$

from initial temperature  $T_0 = 19\text{K}$ . Find out how many time we have to fractional distil the gas mixture to achieve above 98% pure A.

8. Plot (qualitatively) the difference between the molar volumes of liquid and vapour water near critical temperature as a function of temperature.