CHEM352: Physical Chemistry I — Exam II - 9^{th} of Nov, 2018

Name: _____

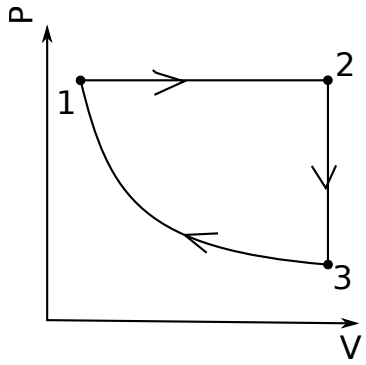
Answer all questions in the space provided. Show all work with ink, no white-outs, use back of the page when needed. Unexplained answers will not receive credit.

The exam consist of 5 questions, 25 points each. Only 4 highest score questions will make the final score.

Total - 100 Pts.

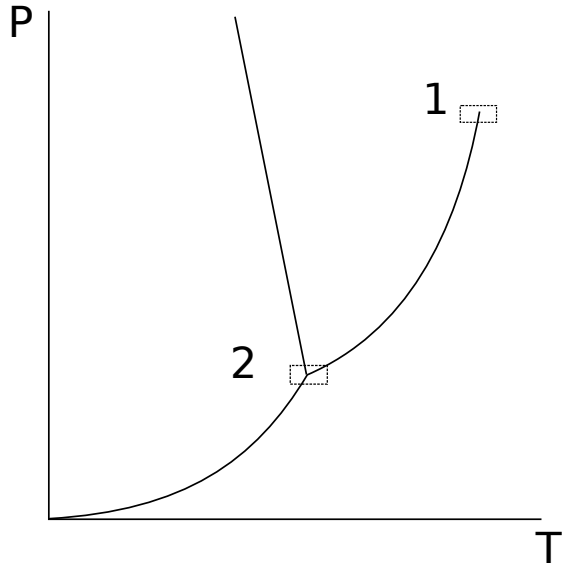
Problem I (Phase diagrams) — 25 Pts

1. One mole of an ideal gas undergoes isobaric ($1 \rightarrow 2$), isochoric ($2 \rightarrow 3$) and isothermal ($3 \rightarrow 1$) transformations, as shown below on 2 dimensional P-V projection of 3-dimensional surface. Please sketch same set of transformations in P-T and V-T projections.

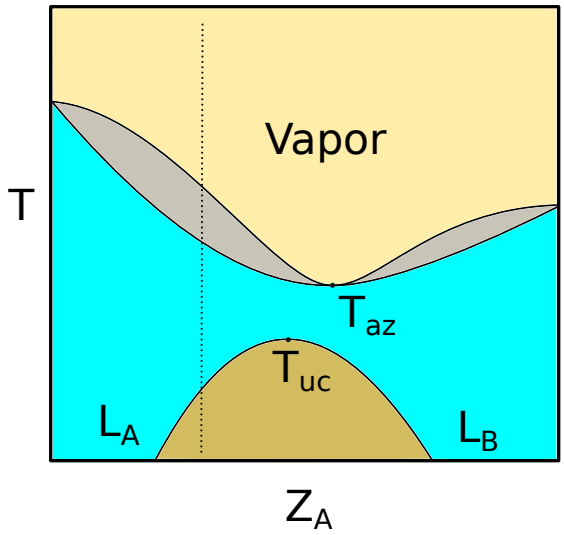


2. Please label all phases, critical temperature and triple point temperature in the generic phase diagram below. Next, please answer:

   (a) What is the value of $\Delta H_{vaporization}$ when you vary P and T along dashed line of rectangle 1.
   (b) What is the value of $\Delta H_{vaporization}$ when you vary P and T along dashed line of rectangle 2.
   (c) Is ΔV_{fusion} positive or negative for the given substance?



3. Two substances A and B are immiscible below T_{uc} and form a minimum boiling point azeotrope, as shown on the diagram in the next page. For a specific mixture composition, we increase a temperature along the dashed line. Please describe all phases present along increasing temperature, temperature ranges they exist and their approximate composition (enriched in substance A or B, when compared to Z_A).


Vapor
T
T_{az}
T_{uc}
L_A
L_B
Z_A

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Problem II (Electrochemistry) 25 Pts

1. The standard reduction potentials for cerium cations are equal:

$$Ce^{3+}(aq) + 3e^- \rightarrow Ce(s) \qquad E^o = -2.483V \tag{1a}$$

$$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq) \qquad E^o = 1.61V \tag{1b}$$

Calculate the E^o for half-cell reaction $Ce^{4+} + 4e^- \rightarrow Ce(s)$. Which of three half-cell reactions are spontaneous?

2. Standard Calomel (Hg_2Cl_2) Electrode (SCE) is defined by following half-cell reaction:

$$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq) \tag{2}$$

Starting from the half-cell of $Hg_2^{2+}(aq) \rightarrow 2Hg(l), E^o = +0.80V$, derive the potential of SCE ($a_{Cl^-} = 1M$) and the electrode immersed in solution of saturated KCl ($a_{Cl^-} = 4.5$M). (Solubility product of calomel is equal $pK_{sp} = 17.9$, Hg_2^{2+} is a cation composed of two mercury ions, each with a formal charge +I.)

3. How does lithium ion battery work? (sketch + 2/3 sentences)

Problem III (Solutions/Mixtures) 25 Pts

1. Starting from Clapeyron equation:
$$\frac{\Delta S_m}{\Delta V_m} = \frac{dP}{dT} \tag{3}$$
where ΔS_m and ΔV_m are changes in molar entropy and molar volume during a phase transition, show that the temperature of sublimation and vaporization of toluene are strongly (exponentially) dependent on applied pressure, whereas fusion temperature depends weakly (linearly).

2. Vapor pressure of acetone is equal 400 Thors at 43^oC and it boils at 56^oC. Please calculate the standard fusion enthalpy and fusion entropy of acetone. What would be boiling temperature of acetone at pressure of 20 atm. We assume that ΔH_{fus} is temperature independent.

3. Let's assume we have a dilute mixture of a solute A in acetone. Explain on the molecular level to which component of the solution Henry's and Raoult's law are applicable. If the Raoult's Law is valid for all range of composition, what properties of A must be? Propose a molecule.

Problem IV (Solutions/Solutes) **25 Pts**

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1. Please explain, in terms of chemical potentials, why addition of a solute changes a freezing and boiling temperatures of a pure substance?

2. The boiling point elevation K_b and freezing point depression constants K_f for benzene are 2.55 and 5.12 $[K \cdot kg \cdot mol^{-1}]$ respectively. Please calculate a change in standard freezing point (278.6 K) and standard boiling point (353.3 K) of 250 g of benzene if we dissolve a 17 g of substance with a molar mass of 340 g/mol. What will be the osmotic pressure pressure of the solution, if density of benzene is equal 0.876 g/cm^3? Assume activity coefficient 1.

3. What's the activity coefficient of the solute, if the temperature of freezing of the solution changed by $\frac{\pi^2}{10}{}^oC$?

Problem V (Electrolyte solutions) **25 Pts**

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1. Solubility product of $PbCl_2$ in water is $1.6 \cdot 10^{-5}$. Using Debye-Hückel limiting law (below), calculate the solubility of $PbCl_2$ in water. The $\gamma_{\pm}$ converges after 4 iterations.

$$\ln \gamma_{\pm} = -1.173|z_+ \cdot z_-|\sqrt{\frac{I}{m_o}} \tag{4}$$

2. $PbCl_2$ dissolves better in higher temperatures. What is responsible for incresed solubility?