MIDTERM #2 EXAMINATION - April 15th, 16th, 2020
Chemical Engineering 140
100 Points
Spring 2020

INSTRUCTIONS
You have 130 minutes to complete this exam and submit your answers to Gradescope once the quiz is submitted on bCourses (2 hour exam time, 10 minute upload time). If you have trouble uploading to Gradescope, send a pdf file of your solutions to Prof. McCloskey (bmcclosk@berkeley.edu).

Time Penalty: 3 pts. per minute late (e.g., turning in your exam 135 minutes after completing the bCourse quiz will result in a 15 point deduction).

Place name and SID on the first page of your submission.

Open notes and book. Equation solvers (Matlab, Wolfram, Excel, etc.) are allowed.

If you use Matlab or other software to solve a problem, clearly identify the equation, boundary conditions, or other parameters you input into the software and indicate that you used the software to calculate a final answer. No need to submit code with your response.

No internet searches allowed.

Completion on a tablet or on paper is allowable. Please upload your solution in proper order (solution to problem 1 first, problem 2 second, etc.).

Show all of your work, keep it legible. BOX ALL ANSWERS if numerical solution or equation is requested.

Read each problem statement carefully, particularly the long ones.

Ideal gas constant:
$R = 8.314\ J\ mol^{-1}\ K^{-1}$; $8.205 \times 10^{-5}\ m^3\ atm\ mol^{-1}\ K^{-1}$

1. [12.5 pts] Please answer the following True or False questions.
   a. [2.5 pt] dG = 0 kJ/mol for any system at equilibrium. (True or False)

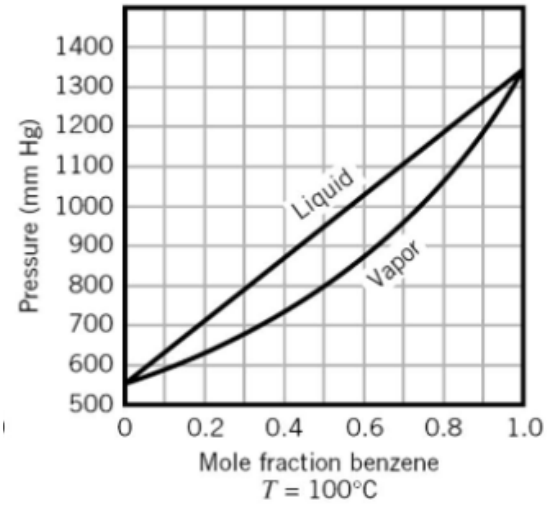
   b. [2.5 pt] The Pitzer acentric factor, ω, is a thermodynamic parameter dependent on molecular geometry and polarity that measures how much the thermodynamic properties of a molecule deviates from the Principle of Corresponding States. (True or False).

   c. [2.5 pt] To correct for non-idealities, Raoult's law is modified using an activity coefficient for the liquid phase and a fugacity coefficient for the vapor phase. (True or False)

   d. [2.5 pt] Benzene and toluene exist in vapor-liquid equilibrium. According to the Gibbs Phase rule, there are two degrees of freedom for this system. (True or False)

   e. [2.5 pt] At modest pressures (<10 atm), the ideal gas law typically underestimates the real pressure we would measure for a given specific molar volume of highly polar gas. (True or False)

2. [7.5 pts] Take the following binary P_{xy} diagram for benzene and toluene in equilibrium at T = 100 °C.



   a. [2.5 pts] If the mole fraction of benzene in the mixture is 0.5, what is the molar composition of the vapor ($y_{benzene}$, $y_{toluene}$) and liquid ($x_{benzene}$, $x_{toluene}$) at 900 mmHg?

   b. [2.5 pts] Benzene is more volatile than toluene. (True or False)

   c. [2.5 pts] The pressure at which we observe the dew point of a 80:20 mixture of benzene:toluene is 1190 mm Hg at 100 °C. (True or False)

3. [9 pts] For a given substance in vapor-liquid equilibrium, the following relationship between the vapor pressure, P_{sat} (in atm), and the temperature, T (in K), is known:

$$dP_{sat}/dT = 4900P_{sat}/(T^2)$$

a. [3 pts] What are the units of '4900' as written in the equation?

b. [3 pts] What is the enthalpy of vaporization, $\Delta H_{vap,}$ in kJ/mol ?

c. [3 pts] For this substance, it is known that at T =10°C, P_{sat} = 0.0123 atm. What is the substance's vapor pressure, P_{sat}, at T = 30 °C (in atm)?

4. [35 pts] Consider the production of chlorine gas (Cl_2) from the oxidation of hydrogen chloride (HCl).

$$4HCl_{(g)} + O_{2\,(g)} \rightleftarrows 2Cl_{2\,(g)} + 2H_2O_{(g)}$$

The free energy of formation at STP of HCl is -95.3 kJ/mol and the free energy of formation at STP of H_2O in the vapor phase is -228.6 kJ/mol. The enthalpy of this reaction is -60 kJ/mol of oxygen gas consumed. The forward reaction (production of $Cl_{2\,(g)}$) has a rate constant, k_f [mol m^{-3} s^{-1} atm^{-5}], and the reverse reaction (consumption of $Cl_{2\,(g)}$) has a rate constant, k_b [mol m^{-3} s^{-1} atm^{-4}]. The equilibrium constant of the reaction, K_{eq}, at 200°C is 13.5 atm^{-1}. This process is carried out in a plug flow reactor (PFR) over a copper chloride catalyst. The inlet stream is stoichiometric, i.e. 4 mol/s HCl and 1 mol/s O_2, and the reactor has a volume of 250 m^3.

(a) [5 pts] What is the equilibrium constant, K_{eq}, for this reaction at 450°C? We can reasonably assume that this temperature is far from ideal conditions.

(b) [5 pts] Assuming that the reaction follows elementary kinetics (i.e., the reaction order of each species is its stoichiometric coefficient), propose an expression for the HCl rate of reaction in terms of species mol fractions, total reactor pressure, and the rate constants, k_f and k_b. Is it reasonable to assume that this reaction in the PFR can be described by an elementary rate law? Why or why not?

(c) [10 pts] The PFR is operating at 450°C and the volume ensures that equilibrium is established between products and reactants at the reactor outlet. What is the operating pressure of this PFR if the measured conversion of HCl is 0.5?

(d) [15 pts] Now consider instead that the reaction is irreversible (i.e. HCl cannot reform after reacting, k_b=0) and has a rate constant k = 1.0 mol m^{-3} s^{-1} atm^{-5}. Using the same elementary rate law assumption as in b), what is the HCl reaction rate expression in terms of species mol fractions, total pressure, and rate constant, k? Given the same inlet flows and reactor volume described in the problem statement, what will be the outlet conversion of HCl if the operating pressure, P = 1 atm? What volume would be needed for 95% conversion of HCl?

5. [35 pts] 8800 kg (2.0×10^5 mols) of pure carbon dioxide (CO_2) are fed into a 150 m^3 cryogenic tank that operates at -45 °C, which is slightly above CO_2's triple point of -56.7 °C. You inspect the tank and realize that no pressure relief valve, a common safety measure to guard against overpressurization, is installed. You find the tank's manual and see that it is rated to a pressure of 250 psi (i.e., it can hold a maximum of 250 psi pressure). As a good chemical engineer, you are concerned that the CO_2 pressure could result in a catastrophic failure of the tank, particularly if the refrigerator keeping the tank at -45° C fails on a hot summer day (say 40°C, or 104 °F). Some useful properties of CO_2, including its qualitative phase diagram, are provided below. The ideal gas law can be assumed to describe the PVT properties of gas phases for this problem.

a. [10 pts] At -45 °C, in what phase does the CO_2 exist (purely liquid, purely gas, solid, vapor and liquid, etc.), and explain your reasoning with relevant calculations. What is the pressure, in psi, of the tank at -45°C?

b. [10 pts] At 40 °C, in what phase does the CO_2 exist (purely liquid, purely gas, solid, vapor and liquid, etc.), and explain your reasoning with relevant calculations. What is the pressure of the tank, in psi, at 40°C? Should you be concerned about the tank exploding?

c. [15 pts] You know that CO_2 dissolves quite readily in water, so you now consider filling a small fraction of the tank with water as a safety measure to reduce the total amount of CO_2 in the gas phase (and hence reduce the pressure). What would the total pressure of the 150 m^3 tank be if you add 10000 kg (5.555×10^5 mols) of H_2O to the 8800 kg (2.0×10^5 mols) CO_2 at 40 °C? Does your idea reduce the pressure compared to the case where the tank is only filled with 8800 kg pure CO_2 at 40 °C? Assume that the water and CO_2 behave as an ideal mixture.

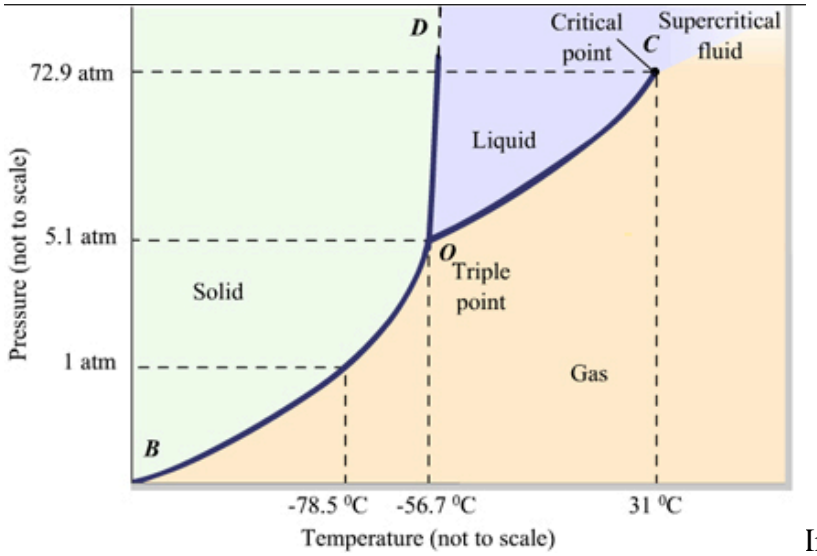
Antoine's equation parameters for CO_2 where P^* is in mm Hg, T is in °C (valid from -62 to 31°C):

$$log_{10}(P^*) = A - B/(T + C)$$

A: 7.5322; B: 835.06; C: 268.223

Critical properties of CO_2: T_c=31 °C, P_c= 72.9 atm, $\tilde{V}_c = RT_c/P_c = 3.42 \times 10^{-4}$ m^3/mol

Henry's Law constant for CO_2 in H_2O at 40 °C: 2450 atm, P^*_{H2O}(T=40 °C)= 0.0727 atm



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