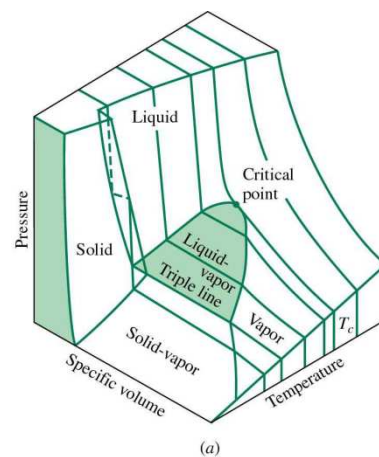
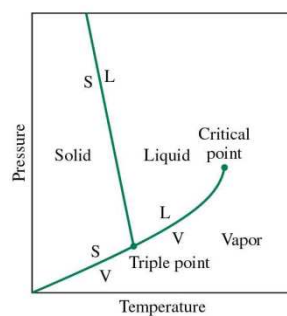


## CHEMICAL THERMODYNAMICS

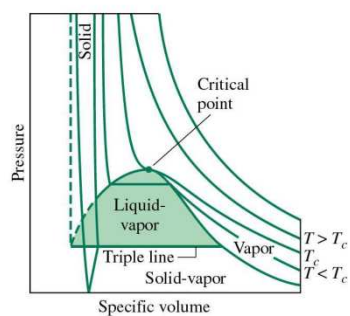
## Handbook of Exercises



(a)



(b)



(c)

Valentim Maria Brunheta Nunes

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"A theory is the more impressive the greater the simplicity of its premises, the more varied the kinds of things that it relates and the more extended the area of its applicability. Therefore classical thermodynamics has made a deep impression on me. It is the only physical theory of universal content which I am convinced, within the areas of the applicability of its basic concepts, will never be overthrown." -- Einstein (1949)

## INTRODUCTION

Thermodynamics it's a discipline that is very important for many engineering degree programs like Chemical and Biochemical Engineering, Environment Engineering or Mechanical Engineering. With the Chemical Thermodynamics course we intend to introduce the principles of thermodynamics, and apply them to systems, that are solids, liquids or gases, with an interest in chemical engineering, don't forgetting environmental issues. This course is also fundamental in the development of important calculation techniques in engineering.

This exercise book will serve to accomplish the lectures, and the problems presented seek to encompass the entire program taught to prepare students for the final evaluations. The resolution of examinations of previous academic years may be also quite helpful for the students.

1<sup>st</sup> Series of Exercises - Gaseous State

1. Calculate the volume occupied by 3 moles of a perfect gas at 2 bar and 350 K.
2. Calculate the final pressure when 1 mole of nitrogen at 300 K and 100 atm is heated, at constant volume, until attaining 500 K.
3. The mass percentage of dry air at sea level is approximately: N<sub>2</sub>, 75%; O<sub>2</sub>, 23.2% and Ar, 1.3%. What are the partial pressures of each component when the total pressure is 1 atm?
4. Calculate the pressure exerted by 1 mole of CO<sub>2</sub> behaving as (a) perfect gas and (b) van der Waals gas, when it is confined in the following conditions: T = 273.15 K and V = 22.414 L (constants of the van der Waals equation: a = 3.592 atm L<sup>2</sup>mol<sup>-2</sup> and b = 4.267×10<sup>-2</sup> Lmol<sup>-1</sup>)
5. Calculate the molar volume of nitrogen at 100 °C and 30.5 atm using:
  - 5.1. The perfect gas equation.
  - 5.2. The van der Waals equation (a = 1.35 dm<sup>6</sup>.atm.mol<sup>-2</sup>; b = 38.6×10<sup>-3</sup> dm<sup>3</sup>.mol<sup>-1</sup>)
  - 5.3. The virial equation:  $Z = 1 - 5.3 \times 10^{-4} p + 4.8 \times 10^{-6} p^2$ , with p in atm.
6. At 300 K and 20 atm, the compressibility factor of a given gas is 0.86. Calculate (a) the volume occupied by 8.2 mmol of gas (b) the approximate value of the second virial coefficient at 300 K.

7. Calculate the pressure exerted by 1 mole of ethane ( $C_2H_6$ ) behaving as:  
 (a) perfect gas; (b) van der Waals gas, when confined in the following conditions: i) 273.15 K and  $V = 22.414$  L; ii) 1000 K and  $100$  cm<sup>3</sup>. Data:  $a = 5.489$  L<sup>2</sup>.atm.mol<sup>-2</sup> and  $b = 6.380 \times 10^{-2}$  L.mol<sup>-1</sup>.
8. Suggest the pressure and temperature for 1 mole of He to be in corresponding states with 1 mole of  $H_2$  at 1 atm and 25 °C. Data:  $P_c(H_2) = 12.8$  atm;  $T_c(H_2) = 33.23$  K;  $P_c(He) = 2.26$  atm;  $T_c(He) = 5.2$  K.
9. The critical constants of methane are  $p_c = 45.6$  atm,  $V_c = 98.7$  cm<sup>3</sup>.mol<sup>-1</sup> and  $T_c = 190.6$  K. Calculate the parameters of the van der Waals equation for this gas and make an estimative of the molecules radius (considered as spheres).
10. A sample of 87 mg of an ideal gas at 0.600 bar duplicates its volume and triplicates its temperature. What will be the final pressure?
11. Two balloons of equal volume and in vacuum are connected by a tube with negligible volume. The first one it's in a thermostatic bath at 200 K and the other in a bath at 300 K; then it is injected in the system 1 mole of an ideal gas. What will be the final number of moles in each balloon?
12. One compound made of nitrogen and oxygen as the following variation of density with pressure at 0 °C:

$p / \text{atm}$	0.333	0.500	0.667	1.000
$(\rho/p)/g.L^{-1} .atm^{-1}$	1.9694	1.9722	1.9746	1.9804

- 12.1. Calculate the molar mass of the compound and suggest the correspondent molecular formula.
- 12.2. Calculate the 2<sup>nd</sup> virial coefficient at 0 °C.
13. Deduce the relation between pressure and density for a perfect gas with molar mass  $M$ . Confirm graphically that dimethyl ether at 25 °C behaves like a perfect gas at low pressures and calculate the correspondent molar mass of gas.

$p/\text{torr}$	91.74	188.98	273.3	452.8	639.3	760
$\rho/\text{g.L}^{-1}$	0.225	0.456	0.664	1.062	1.468	1.734

## 2<sup>nd</sup> Series of Exercises - The First Law of Thermodynamics

14. Two moles of an ideal gas at 500 K are isothermally and reversibly compressed until a final volume that is 1/10 of the initial volume. Calculate: (a)  $\Delta U$  (b)  $\Delta H$  (c) work done by the gas (d) heat absorbed by the gas.
15. Two moles of an ideal gas for which  $C_p = 40 \text{ JK}^{-1}\text{mol}^{-1}$  are heated from 300 to 400 K, (a) at constant pressure and (b) at constant volume. Calculate in each case (i)  $\Delta U$ , (ii)  $\Delta H$ , (iii) work done by the gas and (iv) heat absorbed by the gas.
16. One mole of an ideal gas expands from 10 L and 0 °C to 20 L and 100 °C. Taking  $C_V = 20 \text{ JK}^{-1}\text{mol}^{-1}$ , calculate  $\Delta U$ ,  $W$  and  $Q$  for each of the

following alternative steps for the whole process: (a) Isothermic and reversible expansion at 0 °C from 10 L to 20 L, followed by a constant volume heating until 100 °C and (b) Heating of 10 L at constant volume until 100 °C, followed by an isothermic and reversible expansion until 20 L.

17. A given quantity of an ideal gas occupies 1 dm<sup>3</sup> at 1 atm and 300 K. It is subject to the following transformations:

- (a) Heated at constant pressure until attaining the volume of 2 dm<sup>3</sup>.
- (b) Heated at constant volume of 2 dm<sup>3</sup> until the pressure attains 2 atm.
- (c) Cooled at constant pressure until the volume decreases to 1 dm<sup>3</sup>.
- (d) Cooled at constant volume until the pressure attains 1 atm.

Calculate the sum for the 4 steps for (i)  $\Delta U$ , (ii)  $\Delta H$ , (iii)  $Q$  e (iv)  $W$

18. A sample of 4.5 g of methane occupies 12.7 L at 310 K. Calculate the work done by the gas when it expands isothermally against an external constant pressure of 200 torr until the volume increases 3.3 L. Calculate the work if the expansion was reversible.

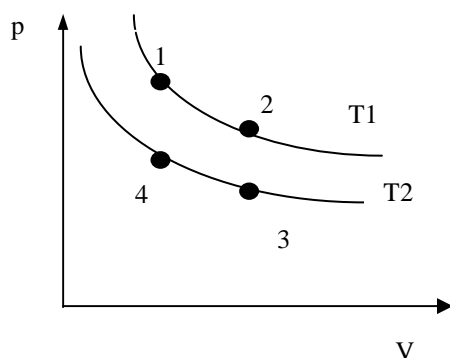
19. Two moles of a gas suffers a reversible and isothermic expansion at 300 K from 1 dm<sup>3</sup> to 10 dm<sup>3</sup>. Calculate the work considering (a) a perfect gas (b) the gas obeys the van der Waals equation, with  $a = 1.36$  atm dm<sup>6</sup> mol<sup>-2</sup> e  $b = 3.183 \times 10^{-2}$  dm<sup>3</sup> mol<sup>-1</sup>.

20. Write an expression for  $dV$ , considering  $V$  as a function of  $p$  and  $T$ . Deduce an expression for  $d/nV$  in terms of the isobaric thermal expansion coefficient and the isothermic compressibility coefficient.

21. In order to project a given refrigerator we need to know the decrease of temperature due to the adiabatic expansion of a refrigerant gas. For a given Freon,  $\mu_{JT} = 1.2 \text{ K atm}^{-1}$ . What is the decrease of pressure necessary to produce a decrease of temperature of 5.0 K?
22. Calculate the amount of heat we have to furnish to 500 g of  $\text{O}_2$  in order to increase the room temperature from 298 K to 500 K, at constant pressure, knowing that:

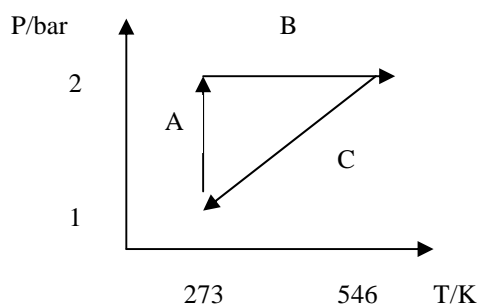
$$C_p(\text{O}_2) = 7.16 + 1 \times 10^{-3} T - 0.40 \times 10^5 / T^2 \text{ cal K}^{-1} \text{ mol}^{-1}$$

23. Consider one mole of nitrogen ( $C_p = 29.4 \text{ JK}^{-1} \text{ mol}^{-1}$ ) at 300 K and 1 atm that suffers a reversible adiabatic compression until 400 K. Calculate:
- The final pressure
  - Work,  $W$ , heat,  $Q$  and the internal energy change of the gas.
24. The following figure shows two reversible processes 1-2-3 and 1-4-3 in which a mole of Freon changes from state  $T_1, p_1$  to the state  $T_2, p_3$ . The



curves  $T_1$  and  $T_2$  are isotherms, and the vertical lines are isochoric ( $V$  constant). Show that the heat involved in the two processes is different, assuming that the Freon is a perfect gas.

25. Consider a monoatomic perfect gas ( $C_V = 3/2 R$ ) that undergoes the following transformation:

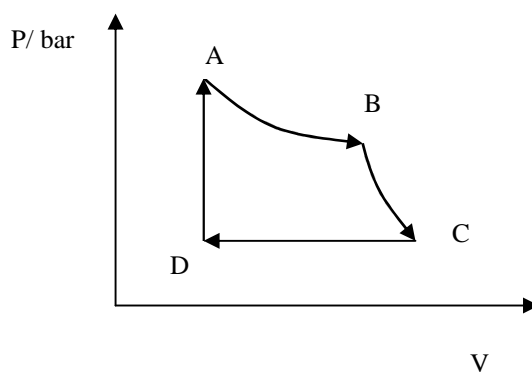


25.1. From the  $p,T$  diagram obtain the correspondent  $p,V$  diagram

25.2. Complete the next table:

	A	B	C	cycle
$\Delta U$				
Q				
W				

26. One kmol of perfect gas undergoes a cyclic process with four steps as shown in the  $p,V$  diagram. The gas is subject to the following reversible steps: i)  $A \rightarrow B$ : isothermic expansion at 600 K from 5 bar to 4 bar; ii)  $B \rightarrow C$ : adiabatic expansion to 3 bar; iii)  $C \rightarrow D$ : cooling at constant pressure; iv)  $D \rightarrow A$ : cooling at constant V. Assuming  $C_p = 30 \text{ J.K}^{-1}.\text{mol}^{-1}$  and constant, calculate Q, W,  $\Delta U$  and  $\Delta H$  for each step and for the cycle.





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### 3<sup>rd</sup> Series of Exercises - Thermochemistry

27. At 300 K the combustion enthalpy of  $\text{Mo}(\text{CO})_6$  (s) is  $\Delta H_c^\circ = -2115.8$   $\text{kJmol}^{-1}$ . Calculate the standard enthalpy of formation of  $\text{Mo}(\text{CO})_6$  (s) knowing that  $\Delta H_f^\circ(\text{CO}_2, \text{g}) = -393.15$   $\text{kJmol}^{-1}$  and  $\Delta H_f^\circ(\text{MoO}_3, \text{s}) = -745.1$   $\text{kJmol}^{-1}$ . At 300 K the enthalpy of sublimation of  $\text{Mo}(\text{CO})_6$  (s) is 74  $\text{kJmol}^{-1}$  and the enthalpy of combustion of  $\text{CO}(\text{g})$  is  $-283.5$   $\text{kJmol}^{-1}$ . Calculate the enthalpy for the reaction of decomposition at 300 K:



Between 300 and 700 K the mean heat capacities are:

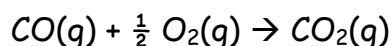
$$C_p [\text{Mo}(\text{CO})_6 (\text{g})] = 247.9 \text{ JK}^{-1}\text{mol}^{-1}$$

$$C_p [\text{Mo}(\text{s})] = 25.0 \text{ JK}^{-1}\text{mol}^{-1}$$

$$C_p [\text{CO}(\text{g})] = 30.1 \text{ JK}^{-1}\text{mol}^{-1}$$

Calculate the enthalpy for the decomposition reaction at 700 K.

28. Calculate the enthalpy change for the following reaction:



at 500 K and 1 atm, knowing that the mean heat capacities are:  $\text{CO}$ :  $C_p = 7.02$   $\text{calmol}^{-1}\text{K}^{-1}$ ;  $\text{O}_2$ :  $C_p = 7.20$   $\text{calK}^{-1}\text{mol}^{-1}$ ;  $\text{CO}_2$ :  $C_p = 9.72$   $\text{calK}^{-1}\text{mol}^{-1}$  and that at 298.15 K we have:  $\Delta H_f^\circ(\text{CO}_2, \text{g}) = -393.5$   $\text{kJmol}^{-1}$  and  $\Delta H_f^\circ(\text{CO}, \text{g}) = -110.5$   $\text{kJmol}^{-1}$ .

29. Calculate the standard enthalpy of combustion of methane at 533 K. At 298.15 K the following data is given:  $\Delta H^{\circ}_c = -0.89 \text{ MJmol}^{-1}$ ;  $\Delta H^{\circ}_{vap}(\text{H}_2\text{O}) = 44 \text{ kJmol}^{-1}$ . In this temperature interval, the heat capacities are (in  $\text{calK}^{-1}\text{mol}^{-1}$ ):

$$C_p(\text{CO}_2) = 10.57 + 2.1 \times 10^{-3} T - 1.80 \times 10^5 / T^2$$

$$C_p(\text{H}_2\text{O}) = 7.30 + 2.46 \times 10^{-3} T$$

$$C_p(\text{CH}_4) = 3.381 + 18.044 \times 10^{-3} T - 4.3 \times 10^{-6} T^2$$

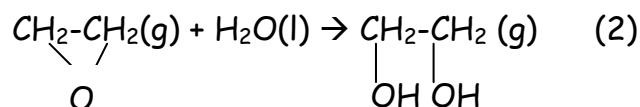
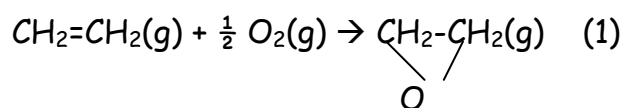
$$C_p(\text{O}_2) = 7.16 + 1.0 \times 10^{-3} T - 0.40 \times 10^5 / T^2$$

30. The standard enthalpy of combustion of naphthalene is  $-5157 \text{ kJmol}^{-1}$ . Calculate the standard enthalpy of formation, knowing that the standard enthalpies of formation of water and carbon dioxide are, respectively,  $-285.83$  and  $-393.51 \text{ kJmol}^{-1}$ .
31. When 120 mg of naphthalene,  $\text{C}_{10}\text{H}_8$ , are burned in a combustion calorimeter, the temperature raises  $3.05 \text{ }^{\circ}\text{C}$ . What is the increase of temperature when 100 mg of phenol,  $\text{C}_6\text{H}_5\text{OH}$ , are burned in the same conditions? The enthalpies of combustion are:

$$\Delta H^{\circ}_c(\text{naphthalene}) = -5157 \text{ kJmol}^{-1}$$

$$\Delta H^{\circ}_c(\text{phenol}) = -3054 \text{ kJmol}^{-1}$$

32. Consider the reaction of formation for ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ) from ethylene oxide ( $\text{C}_2\text{H}_4\text{O}$ ), used at industrial level to produce that compound, by oxidation at air, and at high temperatures, in the presence of silver:



32.1. Explain what you mean by standard enthalpy of formation of a compound.

32.2. Calculate the standard enthalpy of reaction (2) at 200 °C, knowing that at 298.15 K:

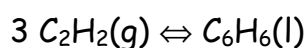
	$\Delta H_f^\circ$ (kcalmol <sup>-1</sup> )	$C_p$ (calmol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H_{vap}^\circ$ (kcalmol <sup>-1</sup> )
C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> (l)	-108.58		14
C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> (g)		16	
C <sub>2</sub> H <sub>4</sub> O(g)	-12.19	14.3	
H <sub>2</sub> O(l)	-68.317	18	

33. Natural Gas, composed essentially of methane, is furnished to a burner at 25 °C. Knowing that one of the products of reaction is H<sub>2</sub>O(g), calculate the maximum temperature that can be obtained in the following conditions:

33.1. 20% of excess air at 25 °C

33.2. The stoichiometric air pre heated at 200 °C

34. Find (in literature) the standard enthalpies of combustion of acetylene (gas) and benzene (liquid) at 298.15 K, and calculate at the same temperature  $\Delta H_r^\circ$  for the following reaction:



35. Calculate the standard molar enthalpy of formation of gaseous propane (a very important combustible) at 1 bar and 298.15 K, knowing that  $\Delta H_c^\circ(\text{C}_3\text{H}_8, \text{g}) = -2220 \text{ kJmol}^{-1}$ ,  $\Delta H_f^\circ(\text{H}_2\text{O}, \text{l}) = -285.83 \text{ kJmol}^{-1}$  and  $\Delta H_f^\circ(\text{CO}_2, \text{g}) = -393.51 \text{ kJmol}^{-1}$
36. Considering the following data for water,  $\Delta H_{fus}^\circ(273.15 \text{ K}) = 333.5 \text{ J.g}^{-1}$ ,  $\Delta H_{vap}^\circ(373.15 \text{ K}) = 2255.2 \text{ J.g}^{-1}$ ,  $C_p(\text{H}_2\text{O}, \text{s}) = 1.975 \text{ J.g}^{-1}.\text{K}^{-1}$ ,  $C_p(\text{H}_2\text{O}, \text{l}) = 4.185 \text{ J.g}^{-1}.\text{K}^{-1}$  and  $C_p(\text{H}_2\text{O}, \text{g}) = 1.860 \text{ J.g}^{-1}.\text{K}^{-1}$ , calculate:
- 36.1. The amount of heat required to raise the temperature of 1 mole of water from  $-5$  to  $120 \text{ }^\circ\text{C}$ , at constant pressure.
- 36.2. The heat of sublimation of water,  $\Delta H_{subl}^\circ$ , at  $-5 \text{ }^\circ\text{C}$ .

#### 4<sup>th</sup> Series of Exercises - The Second Law of Thermodynamics

37. Calculate the entropy change of the system, the surroundings and the Universe, when 14 g of  $\text{N}_2(\text{g})$  at 298.15 K and 1 bar double they volume,
- (a) In an isothermic and reversible expansion
  - (b) In an isothermic and irreversible expansion against  $p_{ext} = 0$
  - (c) In an adiabatic and reversible expansion (comment this last result!)
38. Calculate the entropy change when 1 mole of an ideal gas, for which  $C_p = 40 \text{ JK}^{-1} \text{ mol}^{-1}$ , initially at 273 K:
- (a) Is heated at constant  $p$  until 373 K
  - (b) Is heated at constant  $V$  until 373 K
  - (c) Is adiabatically and reversibly compressed until the temperature attains 373 K

39. On an isolated recipient it was mixed, at constant pressure, 500 g of water at 80 °C with 1000 g of water at 10 °C. Calculate the final temperature of the mixture and the entropy change resulting from this process.

40. The molar heat capacity, at 1 atm, of solid magnesium, between 0 °C and 600 °C is given by:

$$C_p(\text{JK}^{-1}\text{mol}^{-1}) = 26.0 + 5.46 \times 10^{-6} T - 28.6 \times 10^{-4} T^{-2}$$

Calculate the entropy change when 1 mole of metal is heated from 27 °C to 227 °C at 1 atm.

41. Calculate the entropy change, per mole, when cadmium vapor at 767 °C and 1 atm is heated until 1027 °C and compressed to a final pressure of 6 atm. Assume the behavior of an ideal monoatomic gas ( $C_p = 5/2 R = 20.8 \text{ JK}^{-1}\text{mol}^{-1}$ )

42. At 1 atm and between 100 and 200 °C the heat capacity of water vapor is given by:

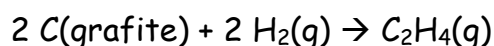
$$C_p (\text{JK}^{-1}\text{mol}^{-1}) = 30.54 + 1.03 \times 10^{-2} T$$

Assuming the ideal behavior calculate  $\Delta H$ ,  $\Delta U$  and  $\Delta S$  when, at 1 atm, 100 g of  $\text{H}_2\text{O}(\text{g})$  at 100 °C are heated until 200 °C.

43. The enthalpy of vaporization of chloroform,  $\text{CHCl}_3$ , is 29.4  $\text{kJmol}^{-1}$ , at the ebullition temperature of 334.8 K. Calculate the entropy of

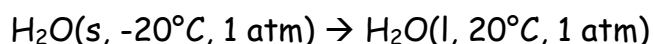
vaporization and compare it with the Trouton's rule. What is the entropy change in the surroundings?

44. Calculate the entropy change for the following reaction:



knowing the absolute entropies at 25 °C:  $S^\circ(\text{grafite}) = 5.7 \text{ JK}^{-1}\text{mol}^{-1}$ ;  
 $S^\circ(\text{H}_2, \text{g}) = 131.2 \text{ JK}^{-1}\text{mol}^{-1}$ ;  $S^\circ(\text{C}_2\text{H}_4, \text{g}) = 221.0 \text{ JK}^{-1}\text{mol}^{-1}$

45. Establish the equation that allows us to calculate the entropy change for the following transformation:



46. A gas for which  $C_p = 5/2 R$  obeys to the equation  $pV = n(RT + Bp)$ , where  $B = 80 \text{ cm}^3\text{mol}^{-1}$ . About 2.5 moles of gas undergoes a Joule-Thomson expansion.

(a) Show that the Joule-Thomson coefficient is given by:

$$\mu_{JT} = -\frac{1}{C_p} \left( \frac{\partial H}{\partial p} \right)_T$$

(b) Calculate the Joule-Thomson coefficient for this gas

(c) Calculate the final temperature when it suffers a Joule-Thomson expansion from 500 K and 50 atm to 1 atm.

(d) For this expansion, calculate i)  $W$  ii)  $\Delta S_{\text{gas}}$  e  $\Delta S_{\text{surr}}$ .

47. We warm up, at  $p=cte$ ,  $70 \text{ m}^3$  a perfect gas, for which  $C_p=7/2 R$ , at 1 bar and  $20 \text{ }^\circ\text{C}$ , until  $25 \text{ }^\circ\text{C}$ , through the heat transfer from a thermal reservoir at  $40 \text{ }^\circ\text{C}$ . Calculate:

- (a) The amount of heat transferred to the gas.  
 (b) The entropy change of the gas, of the reservoir and the total entropy change. Make a comment on the results.

48. Calculate the entropy change of water and surroundings when it freezes 1 mole of  $\text{H}_2\text{O}$  supercooled at  $-10 \text{ }^\circ\text{C}$  and 1 bar. Data:  $C_p(\text{H}_2\text{O}, l) = 75.312 \text{ JK}^{-1}\text{mol}^{-1}$  and  $C_p(\text{H}_2\text{O}, s) = 38.158 \text{ JK}^{-1}\text{mol}^{-1}$ ;  $\Delta H_{fus}^\circ$  of water at  $0 \text{ }^\circ\text{C} = 6026 \text{ Jmol}^{-1}$ .

49. One mole of a perfect gas, for which  $C_p = 38 \text{ JK}^{-1}\text{mol}^{-1}$ , initially at  $25 \text{ }^\circ\text{C}$  and 1 bar is heated and compressed reversibly until  $300 \text{ }^\circ\text{C}$  and 10 bar in three alternative processes:

- (a) Isothermic compression until 10 bar, followed by an isobaric heating until  $300 \text{ }^\circ\text{C}$   
 (b) Isobaric heating until  $300 \text{ }^\circ\text{C}$ , followed by the isothermic compression until 10 bar  
 (c) Adiabatic compression, followed by heating or cooling until  $300 \text{ }^\circ\text{C}$ .

For each of this processes, calculate: i)  $Q$ ,  $W$  e  $\Delta U$  ii)  $\Delta S$

50. The data for heat capacity of sodium sulfate,  $\text{Na}_2\text{SO}_4$  are the following:

T/K	13.74	16.25	20.43
$C_p$ (calK <sup>-1</sup> mol <sup>-1</sup> )	0.171	0.286	0.626

Verify the cubic law of Debye, and calculate the entropy change in the interval of temperatures 0-14 K.

51. One mole of nitrogen, considered as a perfect gas, at 400 K and 5 bar expands adiabatically and reversibly until a final state for which

$$V_{final} = 3 \times V_{initial}.$$

(a) Calculate the final temperature upon expansion ( $C_v = 20.785 \text{ JK}^{-1}\text{mol}^{-1}$ )

(b) Calculate the work done by the gas

(c) Calculate the entropy change of gas

(d) Calculate work done if the expansion was isothermic and reversible.

52. One mole of  $\text{CO}_2(\text{g})$  at 273 K is cooled to  $\text{CO}_2(\text{l})$  at 194.4 K. The cooling is reversible or irreversible by putting the sample in liquid  $\text{H}_2$  at 13.96 K. Calculate the entropy change for this process knowing that  $\Delta H_{vap}^\circ = 23175.2 \text{ J/mol}$  at 194.4 K and  $C_p = 32.22 + 22.18 \times 10^{-3} T - 23.47 \times 10^{-6} T^2$ .

### 5<sup>th</sup> Series of Exercises-Gibbs Energy and Fundamental Equations

53. When a sample of 35 g of a given liquid are isothermally compressed from 1 atm until 300 atm, Gibbs energy increases 12 kJ. Calculate the density of the liquid.

54. Use the Maxwell equations to show that the entropy of a perfect gas depends on volume in the following fashion:  $S \propto R \ln V$

55. Beginning with the differential expression  $dU = TdS - pdV$

(a) Obtain the correspondent expression for  $dH$

(b) Obtain the results of

$$\left(\frac{\partial H}{\partial V}\right)_T \text{ and } \left(\frac{\partial H}{\partial S}\right)_p$$



56. Obtain the thermodynamic equation of state:

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p$$

and show that for a perfect gas:

$$\left(\frac{\partial H}{\partial p}\right)_T = 0$$

57. Knowing that  $dU = Tds - pdV$  and  $H = U + pV$  and  $G = H - TS$ , show that:

$$\left(\frac{\partial H}{\partial p}\right)_S = \left(\frac{\partial G}{\partial p}\right)_T$$

58. Demonstrate that:

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{k_T}$$

59. Demonstrate that:

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

60. Demonstrate that:

$$\left(\frac{\partial T}{\partial V}\right)_U C_V = p - \frac{T\alpha}{k_T}$$

61. Demonstrate that:

$$C_p - C_V = \frac{\alpha^2 TV}{k_T}$$

62. Show that if  $S = S(T,p)$ , then:

$$TdS = C_p dT - T\alpha V dp$$

Calculate now the heat involved when the pressure acting over  $100 \text{ cm}^3$  of mercury at  $0 \text{ }^\circ\text{C}$  is increased in 1 kbar ( $\alpha_p = 1.82 \times 10^{-4} \text{ K}^{-1}$ ). Beginnings with previous equation demonstrate the validity of the equation of exercise 61.

63. Use the Maxwell equations and the Euler chain relation to obtain an expression for

$$\left(\frac{\partial p}{\partial S}\right)_V$$

in terms of the heat capacity, thermal expansion coefficient and isothermic compressibility.

64. In order to calculate the Joule-Thomson coefficient of Fréon-12 there have been several isenthalpic expansions beginning from 10 atm and 322 K.

(a) Obtain the equation:

$$\mu_{JT} = -\frac{1}{C_p} \left(\frac{\partial H}{\partial p}\right)_T$$

(b) In this experiments the following data was measured:

T/K	316.5	313.7	310.9	307.8
P/atm	7.27	5.89	4.55	3.19

Calculate the Joule-Thomson coefficient of Fréon-12 at 10 atm and 322 K.

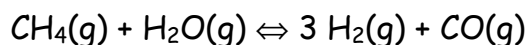
65. Consider the Joule-Thomson coefficient of a van der Waals gas given by:

$$\mu = \left( \frac{\partial T}{\partial P} \right)_H = -\frac{1}{C_p} \left( \frac{\partial H}{\partial P} \right)_T = \left( \frac{\frac{2a}{RT} - b}{C_p} \right)$$

Calculate it for air taking  $a = 1.38 \text{ bar dm}^6 \text{ mol}^{-2}$ ,  $b = 0.0354 \text{ dm}^3 \text{ mol}^{-1}$  and  $C_p = 7/2 R$  at  $T = 200\text{K}$ . In this case, when we assume air as a real gas with intermolecular forces, explain if the air of a tire cool or warms when escaping from a throttle.

### 6th Series of Exercises - Chemical Equilibrium

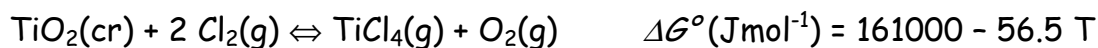
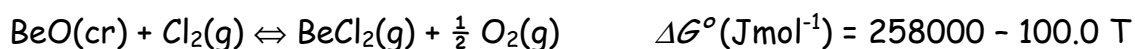
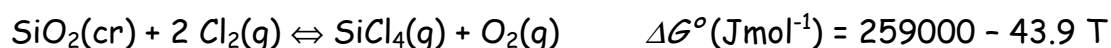
66. Calculate the standard Gibbs energy change for the following reaction at  $25^\circ\text{C}$ :



Use the data of the next table:

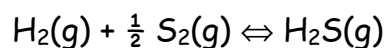
	$\Delta H_f^\circ (\text{kJ mol}^{-1})$	$S^\circ (\text{J mol}^{-1} \text{K}^{-1})$
$\text{CH}_4(\text{g})$	-74.8	186.0
$\text{CO}(\text{g})$	-114.0	197.6
$\text{H}_2(\text{g})$	0	132.0
$\text{H}_2\text{O}(\text{g})$	-241.5	188.6

67. The Gibbs energy change is given, as a function of temperature, for the following reactions:



It will be safe to use silica recipients to store  $\text{TiCl}_4$  or  $\text{BeCl}_2$  at 1 atm and 1000 K? Justify your answer.

68. The variation of  $\ln K_p$  with temperature for the equilibrium:



Is expressed in the following table:

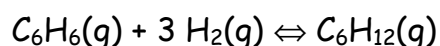
T/K	1023	1218	1362	1473	1667
$\ln K_p$	2.025	1.305	0.902	0.643	0.257

Calculate:

(a) The Gibbs energy change,  $\Delta G^\circ$ , with temperature.

(b) The value of  $\Delta S^\circ$  at 1400 K.

69. For the hydrogenation reaction of benzene to obtain cyclohexane:

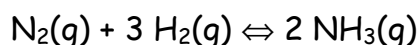


at 1 atm and temperatures from 223 °C and 276 °C, it was proposed the following equation:

$$\ln K_p = 9590/T - 9.9184 \ln T + 0.002285 T + 8.565$$

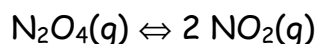
Calculate the enthalpy change,  $\Delta H^\circ$ , at 260 °C.

70. For the reaction:



Calculate the equilibrium constant,  $K_p$ , at 25 °C, knowing that  $\Delta G^\circ_f(\text{NH}_3, \text{g}) = -16.45 \text{ kJmol}^{-1}$ .

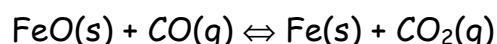
71. At 1 atm and 60 °C  $\text{N}_2\text{O}_4$  exists 50% dissociated. At 100 °C the dissociation percentage is 79%. The reaction is:



- (a) What sign is expected for the enthalpy of dissociation?
- (b) Calculate the enthalpy of dissociation,  $\Delta H^\circ$ .
- (c) Explain the influence of pressure in the equilibrium.

72. The standard Gibbs energy of formation of  $\text{NH}_3(\text{g})$  is  $-16.5 \text{ kJmol}^{-1}$  at 298 K. What is the Gibbs function,  $\Delta G_r$ , when the partial pressures of  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{NH}_3$  (considered as perfect gases) are respectively 3, 1 and 4 bar? What will be the spontaneous direction for the reaction? Justify.

73. Consider the following reaction that occurs in a metallurgical oven:



For this reaction,  $K_p = 0.900$  at 600 °C and  $K_p = 0.396$  at 1000 °C. Explain the influence of temperature and pressure in this chemical equilibrium.

74. Table below shows the equilibrium constants as a function of temperature for the following decomposition reaction:



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$T/K$	350	400	450	500
$K_p$	$3.98 \times 10^{-4}$	$1.41 \times 10^{-2}$	$1.86 \times 10^{-1}$	1.48

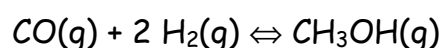
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- (a) Calculate the enthalpy of reaction  
(b) Discuss the influence of pressure and temperature in the equilibrium.

75. The removal of  $\text{NO}_2$  from gaseous effluents of an industrial process is done through the reaction of that compound with  $\text{NH}_3$ , producing water vapor and nitrogen.

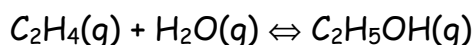
- (a) Explain how you could investigate (at 298 K e 1 atm) the viability of the method.  
(b) Predict the variation of the efficiency of the method with temperature.

76. The reaction between gaseous  $\text{CO}$  and  $\text{H}_2$ , in the presence of a catalyst, is often utilized in industry in the synthesis of a great variety of organic compounds (Fischer-Tropsch process). Consider that a given catalyst allow an adequate velocity for the reaction at 500 °C:



being the reagents furnished in stoichiometric quantities. Knowing that at 773 K  $\Delta G_{r,a}^\circ = 79.16 \text{ kJ mol}^{-1}$ , calculate the minimum pressure necessary for the production of methanol has economic viability (10% of yield).

77. The majority of world's production of ethanol is based on the reaction of hydrolysis of ethylene at high temperatures and pressure, using  $\text{H}_3\text{PO}_4$  as catalyst.



- (a) Find literature values and calculate the conversion of ethylene if the reaction was done at 298 K and 1 bar.
- (b) Knowing that a reactor is feed with a gaseous moisture containing 25% of moles of ethylene and 75% of moles of vapor water, and that the reaction occurs at 125 °C and 1 bar, calculate the final composition of the mixture. At 125 °C,  $\Delta G_r^\circ = 1082 \text{ calmol}^{-1}$ .

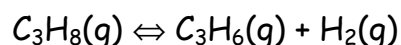
78. The fugacity coefficient of a gas at 200 K and 50 bar is  $\gamma = 0.72$ . Calculate the difference of chemical potential relatively to a perfect gas in the same state.

79. At 200 K the compressibility factor of oxygen changes with pressure according with the next table:

$P/\text{atm}$	1.00	4.00	7.0	10.0	40.0	70.0	100.0
$Z$	0.99701	0.98796	0.9788	0.96959	0.8734	0.7764	0.6871

Calculate the fugacity of oxygen at this temperature and 100 atm.

80. The industrial production of propylene consists in heating propane to high temperatures, according to the reaction:



It is intended to do this reaction in a given reactor with 100 L at constant temperature of 1000 K. The feed of reactor consists in 1 mol of pure propane. Assume that the previous reaction is the only one that occurs in the reactor and that the gaseous mixture is ideal.

- (a) Calculate the amount of propylene in equilibrium. In those conditions  $K_p = 3.0$

- (b) Estimate the pressure in the reactor at equilibrium.
- (c) If the reaction occurs in the same reactor adiabatically, explain how you could calculate the concentrations in equilibrium (the reaction is endothermic).

### 7th Series of Exercises - Phase Equilibrium in Pure Substances

81. Apply the Gibbs Phase Rule to the following systems:

- (a) Vapor in equilibrium with the pure liquid in a sealed cylinder.
- (b) Reaction equilibrium:  $2 \text{Fe}(s) + 3/2 \text{O}_2(g) + x \text{H}_2\text{O}(l) \leftrightarrow \text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O}(s)$
- (c) Mixture of  $\text{O}_2$ ,  $\text{H}_2$  and  $\text{H}_2\text{O}$ , at room temperature, in a sealed recipient.

82. With the following data build the phase diagram of iodine:

Triple point:  $t = 113 \text{ }^\circ\text{C}$ ;  $p = 0.12 \text{ atm}$

Critical point:  $t = 512 \text{ }^\circ\text{C}$ ;  $p = 116 \text{ atm}$

Normal fusion point:  $t = 114 \text{ }^\circ\text{C}$

Normal ebullition point:  $t = 184 \text{ }^\circ\text{C}$

Density of solid  $>$  density of liquid

83. Calculate the enthalpy of vaporization of propanone using the following data for the vapor pressure of this substance as a function of temperature:

$t/^\circ\text{C}$	10	20	30	40	50
$P/\text{mmHg}$	115.6	184.6	282.7	421.5	612.6

Compare this value with the Trouton's rule.

84. Knowing that the vapor pressure of  $\text{CCl}_4$  changes with temperature accordingly with the following data:



$t/^{\circ}\text{C}$	10	20	30	40
$P/\text{mmHg}$	56	91	143	216

Calculate the enthalpy of vaporization and make an estimative of the boiling point of carbon tetrachloride at 200 *mmHg*.

85. Calculate the fusion point of ice, at the pressure of 400 atm knowing that the density of ice and liquid water at 273.15 K and 1 atm are, respectively,  $d = 0.9917$  and  $d = 0.9998 \text{ g cm}^{-3}$ . The enthalpy of fusion is  $333.5 \text{ J g}^{-1}$ .

86. The molar volume of a solid substance is  $161.0 \text{ cm}^3 \text{ mol}^{-1}$  at 1 atm and the fusion point of that substance is 350.75 K. The molar volume of that substance in the liquid state at the same temperature and pressure is  $163.3 \text{ cm}^3 \text{ mol}^{-1}$ . Under the pressure of 100 atm the fusion point changes to 351.26 K. Calculate the enthalpy of fusion of that substance.

87. The barometric formula relates the pressure of a gas of molar mass  $M$  at a given altitude,  $h$ , with the pressure  $p_0$ , at sea level:

$$p = p_0 e^{\frac{-Mgh}{RT}}$$

Combine this formula with the Clausius-Clayperon equation, and predict how varies the boiling temperature of a liquid with altitude, at room temperature. Take the room temperature as  $20^{\circ}\text{C}$  and predict the boiling point of water at 3000 meters of altitude.

88. The vapor pressure of solid ammonia is given by:

$$\ln(p / \text{mmHg}) = 23.03 - \frac{3754}{T}$$

and for liquid ammonia we have:

$$\ln(p / \text{mmHg}) = 19.49 - \frac{3063}{T}$$

- (a) Calculate the temperature and pressure of the triple point of ammonia.
- (b) Calculate the enthalpies of vaporization and sublimation.
- (c) Predict the enthalpy of fusion at the triple point.

89. The vapor pressure of a pure liquid, with molecular mass equal to 46, is 350.2 mmHg at 60 °C and 541.4 mmHg at 70 °C. The mean enthalpy of vaporization in that temperature interval is 865 Jg<sup>-1</sup>. Calculate:

- (a) The boiling point of liquid
- (b) The entropy of vaporization at 60 °C.

### 8th Series of Exercises - Solutions Thermodynamics

90. The partial molar volumes of acetone and chloroform in a mixture where the molar fraction of chloroform is 0.4693 are respectively 74.166 and 80.235 cm<sup>3</sup>mol<sup>-1</sup>. Calculate the volume occupied by 1 kg of solution.

91. The excess Gibbs energy of solutions of Methylcyclohexane and tetrahydrofuran (THF) at 303.15 K, is given by:

$$G^E = RT(1-x)[0.4857 - 0.1077(2x-1) + 0.0191(2x-1)^2]$$

where  $x$  is the molar fraction of methyl cyclohexane. Calculate the Gibbs energy of mixture when we prepare a solution containing 1 mole of and 3 moles of THF.

92. At 300 K, the partial vapor pressure of dilute solutions of HCl in liquid  $\text{GeCl}_4$  are:

$x(\text{HCl})$	0.005	0.012	0.019
$P/\text{kPa}$	32.0	76.9	121.8

Shows that this solution obeys the Henry's Law in this interval of compositions, and calculate the Henry's constant of HCl at 300 K.

93. At 90 °C the vapor pressure of toluene is 400 torr and that of o-xylene is 150 torr. What is the composition of a liquid mixture that boils at 90 °C, when the total pressure is 0.5 atm? What is the composition of the vapor produced?

94. The boiling temperature of a solution containing 0.402 g of naphthalene ( $\text{C}_{10}\text{H}_8$ ) in 26.6 g of chloroform is 0.455 °C higher than that of pure chloroform. Calculate the molal ebullioscopy constant of chloroform.

95. Ethylene glycol,  $\text{CH}_2\text{OHCH}_2\text{OH}$ , is a common anti freezing for automobiles. It is soluble in water and non-volatile ( $T_{eb} = 187$  °C). Calculate the freezing point of a solution containing 651 g of this substance in 2505 g of water. It is reasonable to maintain this substance in the automobile's radiator during the summer?  $K_f(\text{H}_2\text{O}) = 1.86 \text{ K mol}^{-1}\text{kg}$ .

96. A sample of 0.5 g of hemoglobin was dissolved in enough water to prepare 100 ml of solution. The osmotic pressure of this solution, measured at 25 °C, was  $1.78 \times 10^{-3}$  atm. Calculate the molar mass of hemoglobin.

97. A sample of heroine,  $C_{21}H_{23}O_5N$  (molar mass = 369 g/mol) dissimulated in lactose,  $C_{12}H_{22}O_{11}$  (molar mass = 342 g/mol) is analyzed in an osmometer. At 25 °C the osmotic pressure of a solution of 1 g of the sample in 100 cm<sup>3</sup> of water is 539 mmHg. Calculate the percentage of heroine in the sample.

98. The osmotic pressure of solutions of polystyrene in toluene was measured at 25 °C, and the pressure was expressed as the height of solution with a density of 1.004 g/cm<sup>3</sup>:

$C$ (g/L)	2.042	6.613	9.251	12.602
$h$ /cm	0.592	1.910	2.750	3.600

Calculate the molar mass of the polymer.

99. A solution containing 25.97 g of a non-volatile organic compound in 500 g of pure water has a vapor pressure of 17.42 mmHg at 20 °C. Knowing that the vapor pressure of water in the same conditions is 17.51 mmHg, calculate the molar mass of the organic compound.

100. A sample of 6 g of urea,  $(NH_2)_2CO$ , in 1 liter of water at 27 °C, shows a osmotic pressure of 250 kPa. Can this solution be considered as ideal? Justify.

101. At 1 atm and 100 °C, the vapor pressure of a solution where it was dissolved 7.45 g of a non-volatile organic compound in 100 g of water, is 0.98 atm.

- (a) Calculate the molar mass of the compound.
- (b) Calculate the boiling point of solution, knowing that the molal ebullioscopy constant of water is  $K_b = 0.513 \text{ K mol}^{-1} \text{ kg}$ .

102. For the binary system acetone(1) + acetonitrile(2), we have the following data at 50 °C:

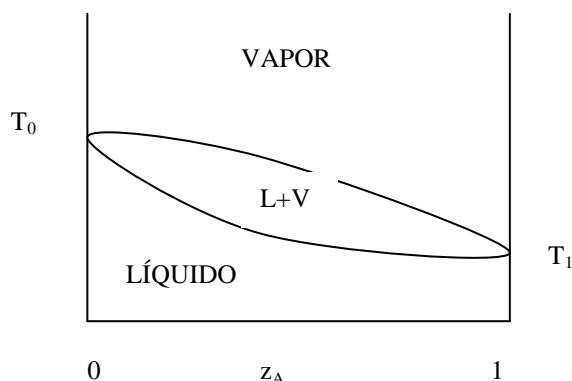
$x_1$	$p_1/\text{mmHg}$	$p_2/\text{mmHg}$
1	615.0	0
0.8	492.0	50.70
0.7	430.5	76.05
0.5	307.5	126.75
0.3	184.5	177.45
0.2	123.0	202.80
0.1	61.5	228.15
0	0	253.50

- (a) Verify if the solution shows an ideal behavior.
- (b) For the solution with  $x_1 = 0.6$ , what is the total vapor pressure and molar fraction of acetone in the vapor pressure?
- (c) Calculate the Gibbs energy of mixture for the solution with  $x_1 = 0.35$ .

103. The vapor pressure of pure bromobenzene and chlorobenzene at 90 °C are respectively 220 mmHg and 98 mmHg. Calculate:

- (a) The vapor pressure of a mixture containing 28.14 g of chlorobenzene and 78.50 g of bromobenzene, at that temperature.
- (b) The molar fraction of bromobenzene in the vapor phase.

104. The phase diagram of a solution containing A and B, at the pressure of 1 atm is displayed in the following figure:



The upper curve can be represented by:  $T = T_0 - (T_0 - T_1)y_A^2$  and the lower curve by:  $T = T_0 - (T_0 - T_1)x_A(2 - x_A)$ . A recipient containing equal number of moles of each component is taken to ebullition.

- (a) What is the composition of vapor when the ebullition begins?  
 (b) The remiscible liquid should be more rich in component A? Justify.

105. The vapor pressure of propyl alcohol in solutions with benzene are:

$$x_1 = 1; p = 44 \text{ mmHg}$$

$$x_1 = 0.924; p = 42.2 \text{ mmHg}$$

$$x_1 = 0.835; p = 39.5 \text{ mmHg}$$

Calculate the activity coefficient of alcohol in the two mixtures and the chemical potential difference of alcohol for  $x_1 = 0.924$ , relatively to an ideal solution at same composition.

106. Carbon tetrachloride (1) forms an azeotropic mixture with methanol (2) at the composition of  $x_1 = 0.45$ . The boiling point of azeotrope is  $55.7^\circ\text{C}$  and the boiling points of pure  $\text{CCl}_4$  and methanol are respectively  $76.75$  and  $64.7^\circ\text{C}$ . Represent in a Temperature-composition diagram and

explain what happens when we try to distill solutions of composition  $x_2 = 0.4$  and  $x_2 = 0.8$ .

107. The vapor pressures of pure benzene and toluene are given by the general equation:

$$\log_{10} p^* (Pa) = \frac{-0.05223 \times A}{T} + B$$

Where the constants A and B are given in the following table:

	A/K	B
Benzene	32295	9.7795
Toluene	39198	10.4549

Supposing the formation of ideal solutions between benzene and toluene, calculate:

- The molar percentage of benzene in a mixture that boils at 97 °C and at the pressure of 1 atm
- The composition of the condensed liquid formed upon the distillation of mixture.

108. Consider the following data for a binary mixture of A and B:

$x_B$	0	0.096	0.120	0.198	0.806	0.849	0.950	1
$p_A$	306	277	269	250	70.7	56.2	18.6	0
$p_B$	0	34.4	42.6	67	228	240	266	280

- Show if the system is ideal or non-ideal.
- Make a diagram considering for A the Henry's law and for B the Raoult's law.
- Calculate the activity coefficient of B in the mixture  $x_B = 0.849$

109. A liquid mixture at 300 K has a vapor pressure of 600 *mmHg* when it contains equal parts of two non-polar components A and B. Estimate the vapor composition in equilibrium with a liquid mixture of A and B at 300 K with 10% of moles of A. Consider for the liquid phase the two suffix Margules equation. At 300 K,  $p_A^* = 500$  torr and  $p_B^* = 460$  torr.

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