

UNIVERSITY CEU SAN PABLO  
SCHOOL OF PHARMACY  
DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY

## ISSUES OF PHYSICAL CHEMISTRY

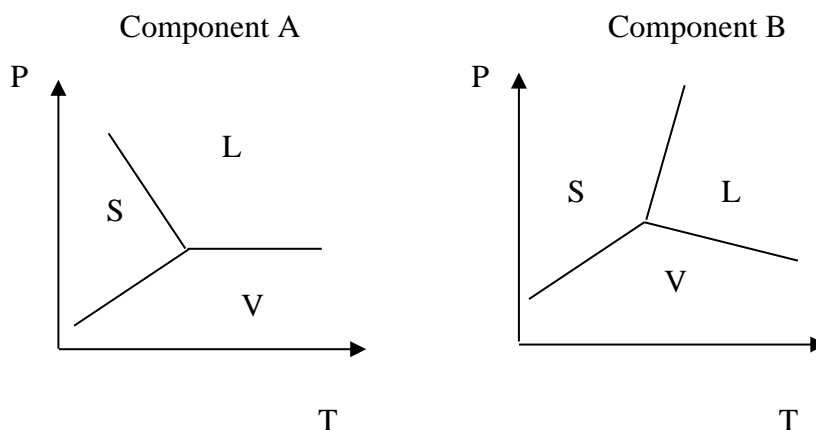
2018-2019

### LESSON 3

10. Certain substance exists in two solid forms, Q and R, as well as in the liquid and vapour phases. The following triple points have been observed:

Temperature (°C)	P (atm)	Phases
10	1	Q, R, vapour
80	10	R, liquid, vapour
50	1000	Q, R, liquid

- a) Plot schematically the PT phase diagram for that substance, indicating the number of phases in each region.
- b) Demonstrate, using the appropriate equations that  $\rho_Q > \rho_R$ , knowing that  $\Delta H$  for  $Q \rightarrow R$  transition is positive.
11. Indicate if  $\Delta H$ ,  $\Delta V$  and  $dP/dT$  is positive, zero or negative in each of the following phase changes:
- liquid-solid
  - liquid-vapour
  - solid-vapour
12. The diagrams of two pure components A and B are as indicated in the following figures:



What will be the sign of the volume changes in the melting and vaporization of components A and B? What conclusions can be drawn from the results obtained?

13. Indicate whether the following statements are true, using the appropriate equations:
- In a single-component system the solid has always higher density than the liquid when the solid-liquid line has a positive slope.
  - The plot of  $\log P$  versus  $1/T$  is always a line of positive slope.
  - The pressure and temperature of the critical point of  $\text{CO}_2$  are 31.1 atm and 311.0 K, respectively while its triple point is at 5.11 atm and 216.8 K. If  $\text{CO}_2$  is progressively heated at constant pressure of 1 atm, to reach 298 K, then  $\text{CO}_2$  is in liquid state.

14.  $T_{\text{ms}}^\circ$  and  $T_{\text{b}}^\circ$  of Ar are 83.8 K and 87.3 K, respectively; its triple point is at 83.8 K and 0.7 atm and the values of the critical temperature and pressure are 151 K and 48 atm. Indicate whether the Ar is in solid, liquid or vapour phase in each of the following conditions:
- 0.9 atm and 90 K
  - 0.7 atm and 80 K
  - 0.8 atm and 88 K
  - 1.2 atm and 86 K
  - 0.5 atm and 84 K

15. Indicate whether the following statements true or false, reasoning the answers:
- In a single-component system the maximum number of phases that may coexist in equilibrium is three.
  - The equation:  $\frac{dP}{dT} = \frac{\Delta\bar{H}}{T\Delta V}$  is an exact equation.
  - Solid water can not exist at 100 °C.
  - In a single-component system, the most stable phase at a given T and P is the phase with the lowest free energy.

16. Could equation  $\ln \frac{P_2}{P_1} = \frac{\Delta\bar{H}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$  be applied to a first-order transition carbon (graphite)  $\rightarrow$  Carbon (diamond)?  
Indicate the approaches considered to obtain the above equation.

17. The following table shows the vapour pressures of water and acetone of solutions in equilibrium at 25 °C:

$x_{\text{Acetone}}^l$	0	0.0333	0.117	0.236	0.420	0.737	1
$x_{\text{Acetone}}^v$	0	0.6230	0.8203	0.8690	0.8817	0.9187	1
$P_{\text{Acetone}} / (\text{mmHg})$	0	38	105	146	164	192	229
$P_{\text{water}} / (\text{mmHg})$	24	23	23	22	22	17	0

- Draw the phase diagram of the total vapour pressure as a function of mole fraction of acetone in the solution and vapour. Identify the different regions of the diagram, indicating the phases present.

b) Calculate the composition of the two phases in equilibrium of a solution consisting of 50 g of acetone and 15.5 g of water at 225 mm Hg, if the pressure is reduced to 100 mmHg.

c) Indicates that changes occur if the pressure is decreased to 25 mmHg.

**Data:**  $M_{\text{acetone}} = 58 \text{ g}\cdot\text{mol}^{-1}$ ;  $M_{\text{water}} = 18 \text{ g}\cdot\text{mol}^{-1}$

18. Two liquids A and B form an ideal solution. Their pure vapour pressures at 303 K are 80 and 30 kPa, respectively.

a) Represent the phase diagram, knowing that when  $x_B^V$  is 0.1 the total pressure is 60 kPa and when  $x_B^V$  is 0.2, the total pressure is 50 kPa

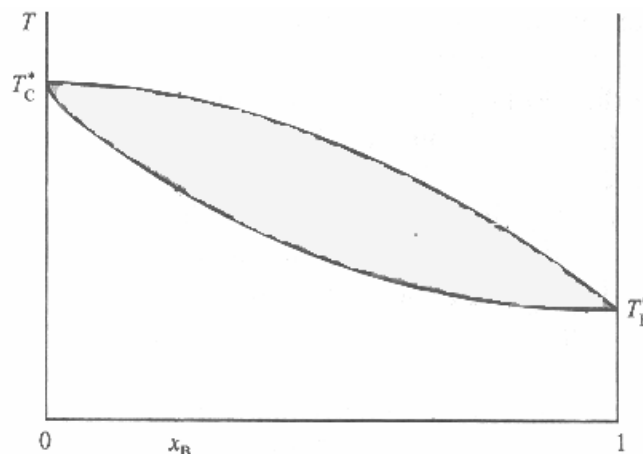
b) Calculate the ratio of two phases are in equilibrium, at 35 kPa, for a total mole fraction of B equals 0.6

19. Indicate the differences in applying the fractional distillation to a mixture of two components with ideal and real behaviour.

20. A solution of the system of the figure with molar fraction of B equal to 0.30 is heated isobarically in a closed container

a) calculate the composition of the first vapour formed

b) calculate the composition of each of the phases when half the moles of liquid is vaporized.



21. Chloroform and ethanol present an azeotrope at atmospheric pressure, of 87.4% of  $\text{CH}_3\text{Cl}$  and with a boiling point of  $53.43^\circ\text{C}$ . The boiling temperatures of chloroform and ethanol are  $61.2^\circ\text{C}$  and  $64.7^\circ\text{C}$ , respectively

a) Describe the azeotropic compound.

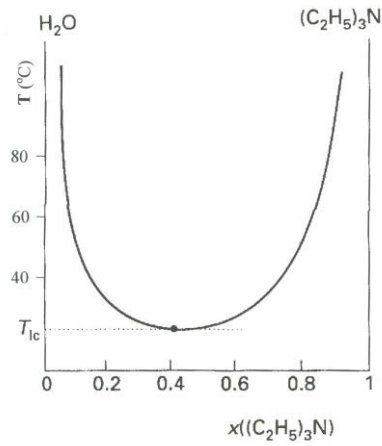
b) Indicate if pure  $\text{CH}_3\text{Cl}$  can be obtained by fractional distillation from a mixture of 30% of  $\text{CH}_3\text{Cl}$

22. Explain, briefly, how the compositions of the phases in equilibrium in a liquid-liquid diagram change with:

a) the overall composition of the system at constant temperature.

b) temperature at constant overall composition.

23. The following diagram of liquid-liquid equilibrium:



Indicate what changes occur in the system when preparing mixtures of compositions  $X_{(\text{C}_2\text{H}_5)_3\text{N}}$  equal to 0.05; 0.30; 0.40 and 0.60, all at  $40^{\circ}\text{C}$  and with the same overall number of moles.