COMPLEMENTARY PROBLEMS OF PHYSICAL CHEMISTRY

2018-19

LESSON 4

19. An ideal solution is comprised of two components, A and B. The vapour pressure of pure A is 125 mmHg at 25 ° C and B is a non-volatile component. A mixture with 1 g B and 20 g A has a vapor pressure of 110 mmHg at 25 ° C. What is the relationship between the molecular weights of A and B?

Solution: $M_A / M_B = 2.72$

20. An aerosol container* contains an (ideal) liquid propellant mixture of A and B in equilibrium with its vapour. If the composition of the liquid is $X_A^l = 0,7$ and $X_B^l = 0,3$. Determine:
a) Vapour pressure at 25 ° C and 50 ° C inside the container
b) The composition of the vapour in equilibrium at 25 ° C and 50 ° C.
c) When the mixture of propellants go outside where the pressure is 1 atm, what phase was found at both temperatures?

Data: $P_A^*(25) = 1.9 \cdot 105$ N $\cdot$ m^{-2}; $T_{b(A)}^o = 276.8$ K; $\Delta Hvap (A) = 4863.12$ cal $\cdot$ mol^{-1};

$P_B^*(25) = 5.85 \cdot 105$ N $\cdot$ m^{-2}; $T_{b(B)}^o = 243.4$ K; $\Delta Hvap (B) = 4615.63$ cal$\cdot$mol^{-1};

1 atm = 101300 N$\cdot$m^{-2}; R = 1.987 cal$\cdot$K$^{-1}\cdot$mol^{-1}

* Fluorinated hydrocarbons as dichlorotetrafluoroethane (A) and chlorodifluoro-methane (B) are used as propellants in aerosol pharmaceutical formulation (pressurized containers that contains the active component suspended in a propellant that can expel the product when the valve is opened)

Solution: a) P (25) = 308,500 N $\cdot$ m^{-2}; P (50) = 569 510 N $\cdot$ m^{-2}

b) $X_A^V(25°C) = 0.43; X_B^V(25°C) = 0.57; X_A^V(50°C) = 0.44; X_B^V(50°C) = 0.56$

c) Vapour

21. At 90 ° C, the vapour pressure of pure toluene and o-xylene are 400 mmHg and 150 mmHg, respectively. What is the composition of the mixture whose boiling point is 90 ° C under a pressure of 0.5 atm? What is the composition of the vapour in equilibrium?
Assume ideal behaviour.

Solution: a) $x_{o-xilene}^L = 0.08$; **b)** $x_{o-xilene}^V = 0,032$

22. The following data are the vapour pressure of water and the molality of sucrose in aqueous solutions measured at 25 ° C. Check if the solvent satisfies Raoult's law. If not calculate solvent activity and activity coefficient.

m (sucrose) /(mol·Kg^{-1})	0.000	0.200	2.000
P / (mm Hg)	23.75	23.66	22.75

Solution: m_{suc} = 0 ⇒ pure H_2O; m_{suc} = 0.200 m ⇒ It follows Raoult's law; m_{suc} = 2.000 m ⇒ It does not follow Raoult's law ($a_{I, water}$ = 0.9579; $\gamma_{I, water}$ = 0.9924)

23. At 23 ºC, a mixture of two components A and B with 74% moles of A is prepared. The total pressure is 303 mmHg with with 74% moles of A in the vapour. Determine:

a) the activity and activity coefficient of each component according to convention I.

b) the activity and activity coefficient of each component according to convention II, considering A the solvent.

c) Describe the system.

Data: $P*_A$ (8ºC)= 112 mmHg; $P*_B$ (23ºC)= 203 mmHg; ΔH_{vap} (A) = 330 cal·mol^{-1}; K_B = 361 mmHg; R = 0.082 l·atm·K^{-1}·mol^{-1} = 1.987 cal·K^{-1}·mol^{-1} = =8.314 J·K^{-1}·mol^{-1}

Solución: a) $\gamma_{A,I}$ = 2.630; $\gamma_{B,I}$ = 1.493; **b)** $\gamma_{A,II}$ = 2.630; $\gamma_{B,II}$ = 0.839

24. Two liquids A and B form non-ideal solutions. At 70 ° C, the vapour pressure of pure A is 280 mm Hg. and for pure B is 650 mm Hg at 30 °C. The total vapour pressure of a solution of 0.5 mole fraction is 500 mm Hg, at 30 ° C and the activity coefficient of B according convention I is 1.3; calculate:

a) The activity coefficient of A in this solution
b) The activity of both components
c) Draw the diagram of vapour pressure versus composition at 30 ° C.

Data: $\Delta \overline{H}_{vap,A}$ =4100 cal·mol^{-1}
R = 0.082 l·atm·K^{-1}·mol^{-1} = 1.987 cal·K^{-1}·mol^{-1} = 8.314 J·K^{-1}·mol^{-1}
Solution: a) $\gamma_{I, A}$ = 1.22; **b)** $a_{I, A}$ = 0.61; $a_{I, B}$ = 0.65

25. The table below show the total pressure and the composition of the solution and of the vapour at 25 ° C:

x_A^L	P (torr)	X_A^v
1	500.0	1
0,985	499.6	0.9881
0,950	506.4	0.9615
0,925	517.4	0.9442
0.9	533.0	0.9287
0,875	552.7	0,9152
0.85	576.1	0.9037
0.75	696.9	0.8744

Determine the activity and the activity coefficient of A and B for a solution with x_A^L = 0.9 according to the Convention I and II.
Data: P_B^* (25 ºC) = 200 torr

Solution: a) $a_{I, A}$ = 0.9899; $\gamma_{I, A}$ = 1.0999; $a_{I, B}$ = 0.1900; $\gamma_{I, B}$ = 1.9001
      b) $a_{II, A}$ = 0.9899; $\gamma_{II, A}$ = 1.0999; $a_{II, B}$ = 0.0950; $\gamma_{II, B}$ = 0.9508

26. At 35 ° C, the vapour pressures of chloroform and ethanol are 295.1 torr and 102.8 torr. At 35 ° C, a solution of chloroform and ethanol with X_{et}^l = 0,200 has a vapour pressure of 304.2 torr and the vapour has a composition X_{et}^v = 0,138. Calculate:
a) γ_I and a_I of chloroform and ethanol in this solution.
b) $\mu_i - \mu_i^*$, for each component of this solution.
Data: R = 0.082 l·atm·K^{-1}·mol^{-1} = 1.987 cal·K^{-1}·mol^{-1} = 8.314 J·K^{-1}·mol^{-1}

Solution: a) $\gamma_{I, chlor}$ = 1.11; $\gamma_{I, etha}$ = 2.04: $a_{I, chlor}$ = 0.888; $a_{I, etha}$ = 0.408
      b) $\mu_{chlor} - \mu_{chlor}^*$ = −72.3505 cal·mol^{-1}; $\mu_{etha} - \mu_{etha}^*$ = −548,1973 cal·mol^{-1}

27. The following data refer to a mixture of equimolar amounts of two substances A and B, at 308.3 K:

P_A = 20,5 KN·m^{-2}

P_B = 15,5 KN·m^{-2}

Calculate:
a) Indicate what kind of deviations respect to Raoult's law present each compound.
b) Represent graphically the vapour pressures of A and B and the total vapour pressure as a function of the mole fraction of B. In the same graph represent the same magnitudes assuming ideal behaviour.
Data: R = 0.082 l·atm·K^{-1}·mol^{-1} = 1.987 cal·K^{-1}·mol^{-1} = 8.314 J·K^{-1}·mol^{-1}

   $P_A^*(308.3\,K)$ = 49.5 K·N·m^{-2}; $P_B^*(308.3\,K)$ = 39.1 K·N·m^{-2}

Solution: $\gamma_{I,A}$ = 0.8282; $\gamma_{I,B}$ = 0.7928 $\Rightarrow$ negative deviations with respect to Raoult's law.

28. Given the following aqueous solution at 298 K:

  a) 0.01 M of $CaCl_2$

  b) 0.10 M of $MgSO_4$

  c) A mixture of $(NH_4)_2SO_4$ 0.5 M with Urea 0.5 M

Calculate:

1) The ionic strength of each of the solutions.

2) The mean ionic activity coefficient in all solutions where possible, using the limiting law of Debye-Huckel.

3) What other method could be used to determine the $\gamma \pm$?

Data: A = 0.51