VIVEKANANDA COLLEGE, THAKURPUKUR

NAAC Accredited Grade—A

STUDY MATERIAL

Subject	: Physical Chemistry
Course Title	: Applications of Thermodynamics II
Topic	: Mathematical Problems & Questions-answers discussion on The Phase Equilibrium Chapter.
Paper	: Physical Chemistry **– 3** **(CODE: CEMA-CC-4-9-TH)**
Semester	: 4th Semester
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Mathematical Problems:

1.Calculate the molal solubility of CO_2 in water at 298 K and a CO_2 pressure of 3.3 $x10^{-4}$ atm, which corresponds to the partial pressure of CO_2 in air. (K = 1.24 x 10^6 torr

Henry's law suggests P = K x_2 where K = Henry's constant and x_2 = mole fraction of CO_2.

x_2 = P / K = 3.3 $x10^{-4}$ x 760 torr / 1.24 x 10^6 torr

= 2.0225 x 10^{-7}

n_2/n_2+n_1 where n_2 = no of moles of CO2 present and n_1 = no of moles of water

n_1 = 1000/18 = 55.555 mole

∴ n_2/n_2+n_1 = 2.0225 x 10^{-7}

Or, n_2 (1-2.0225 x 10^{-7}) = 55.555 x 2.0225 x 10^{-7}

Or, n_2 = 1.1236 x 10^{-5} molal

∴ **Molality of CO_2 present = 1.1236 x 10^{-5} molal**

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2. Liquids A and B form an ideal solution, the vapour pressures of pure A and B are 66 torr and 88 torr respectively. Calculate the composition of the vapour in equilibrium with a solution containing 36 mole percent of A.

From Raoult's law, $p_A = x_A \cdot P^o_A$ = 0.36 x 66 torr =23.8 torr
and
$p_B = x_B \cdot P^o_B$ = 0.64 x 88 torr = 56.3 torr
∴ total pressure $p_A + p_B$ = (23.8+56.3) = 80.1 torr
Composition of A = $x_{A(vap)}$ = 23.8 /80.1 = 0.297 and composition of B = $x_{B(vap)}$ = 56.3/ 80.1 = 0.7028

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3. Calculate the Gibbs free energy and entropy of mixing of 1.6 moles of Argon at 1 atm and 25 ºC with 2.6 moles of nitrogen at 1 atm and 25 ºC. Assume ideal behavior.

ΔG mix(ideal) = nRT $\sum x_i \ln x_i$ = 4.2 mole x 8.314 J $mole^{-1}$K x298 K [(1.6/4.2 ln(1.6/4.2) +2.6/4.2 ln(1.6/4.2)]

= 10405.8024J (-0.3676 – 0.2969)

= 6914.43J

= 6.914J

ΔS mix(ideal) = $- nR \sum x_i \ln x_i$ = - 4.2 mole x 8.314 J mole^{-1} K^{-1}[1.6/4.2.ln(1.6/4.2) + 2.6/4.2.ln(2.6/4.2]

= - 34.9188 x (- 0.3676 – 0.2969) J K^{-1}

= 23.2 J K^{-1}

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4. If 29 mg of N2 dissolves in 1 L of water at 0 ºC and 760 torr N_2 pressure, how much N_2 will dissolve in 1L of water at 0 ºC and 5 atm N_2 pressure?

As per first condition x_{N2} = K.P = K. 760 torr

∙: According to second condition, x'_{N2} = K. 5 x 760 torr

∙: x'_{N2} = 5 x x_{N2} = 5x29mg per L = 145 mg/L

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5. A litre of CO_2. At 15 ºC and 1.00 atm dissolves in 1.00 litre of water at the same temperature when the pressure of CO_2. is 1.00 atm. Compute over which the partial pressure of CO_2. is 150 torr at this temperature.

No of moles of CO_2. present = PV/RT = 1x1 lit.atm/.082lit. atm. K^{-1} mol^{-1} x 288K = 0.04234 mole

Mole fraction CO_2. = .04234/ (.04234 +1000/18) = 7.615 x 10^{-4} = x_2

We know that x_2 = K.P

Or, K = x_2/P = 7.615 x 10^{-4} /1atm = 7.615 x 10^{-4} atm^{-1}

But when partial pressure is 150 torr = 150 / 760 atm, then

x'_2 = K . p_{new} = 7.615 x 10^{-4} atm^{-1} x (150/760) atm = 1.503 x 10^{-4}

Therefore, new concentration of CO2 in water(1lit) = 1.503 x 10^{-4} = / (n'_2 + n_1)

So, (n'_2 +1000/18) x 1.503 x 10^{-4} = n'_2

By solving we get new concentration of CO_2 (n'_2) = 8.351 x 10^{-3} (m)

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6. A phenol + water system separates system into two-liquid phases at a temperature of 60 ºC. The first phase contains 16.8 mass% of phenol, the second phase contains 44.9 % of water by mass. If the system contains 90 g of water and 60 g of phenol, what is the mass of each phase?

Let the weight of the water rich layer = a

·: Weight of phenol rich layer = 150-a

For the first phase: Phenol = 16.8 % by weight and water = 83.2% by weight

For the second phase: Water = 44.9 % by weight and Phenol = 55.1% by weight

By problem, 0.551 x (150 - a) + 0.168 x a = 60

Or, 82.65 – 0.551a + 0.168a = 60

Or, (0.551- 0.168) x a = (82.65-60) = 22.65

Or, 0.383 x a = 22.65

a = 22.65/ 0.383

= 59.138 g.

So, weight of the water rich layer = 59.138 g.

And weight of the phenol rich layer = (150-59.138) g.

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7. A certain solution of benzoic acid in benzene has freezing point 3.1ºC and boiling point of 82.6 ºC at 1 atm pressure. Explain these observations and suggest the structure of the solute particles at two temperatures. [Given: T_f = 278.5 K (normal), Tb = 353 K (normal), K_f = 5.12 kg mol^{-1} , K_b = 2.53 kg mol^{-1} for benzene)

$\Delta T_f = K_f$. Cm and $\Delta T_b = K_b$. Cm also $i_f = (\Delta T_f)_{expt} / (\Delta T_f)_{theo}$; $i_b = (\Delta T_b)_{expt} / (\Delta T_b)_{theo}$

$(\Delta T_f)_{expt}$ = (278.5-276.1) K = 2.4 K = 2.4 ºC

(ΔT_f) theo = $K_f . C_m$ = 5.12 kg. mol^{-1} C_m

·: $i_f = (\Delta T_f)_{expt} / (\Delta T_f)_{theo}$ = 2.4 ºC /5.12 kg. mol^{-1} C_m = 0.46875 ºC / kg. mol^{-1} C_m

$(\Delta T_b)_{expt}$ = (82.6 ºC – 80 ºC) = 2.6 ºC

$(\Delta T_b)_{theo}$ = 2.53 kg.mol^{-1}. C_m

$i_b = (\Delta T_b)_{expt} / (\Delta T_b)_{theo}$ = 2.6 ºC / 2.53 kg.mol^{-1}. C_m = 1.02766 ºC / kg. mol^{-1} C_m

∴ i_b / i_f = (1.02766 ºC / kg. mol^{-1} C_m)/ (0.46875 ºC / kg. mol^{-1} C_m) = 2.19

Higher i means number of particles are higher. Hence, a greater number of particles are present near the boiling point in comparison to that near the freezing point.

i_f / i_b is just nearly half of the i_b. At low temperature benzoic acid remains as associated form and probably as dimer and dissociates as monomer at higher temperature.

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8. The melting point of phenol is 40 ºC. A solution containing 0.172 g. acetanilide in 12.54 g. phenol freezes at 39.25 ºC. Calculate the cryoscopy constant and the latent heat of fusion of phenol.

Molecular formula of acetanilide = $C8H_9NO$ = 8x12+9x1+ !4+16 = 135;

Δ T_f = K_f . Cm

Or, (40-39.25) ºC = 0.75 ºC

Or, $K_{f.}$ Cm = 0.75 ºC

Or, $K_{f.}$ = 0.75 ºC / Cm

Cm = 1000x.172/(135x12.54) = 0.1016 (m)

$K_{f.}$ = .75/.1016 = 7.3818 K mol g^{-1}

K_f =R $T^2{}_f$ / 1000 .L_f

L_f = R $T^2{}_f$ / 1000 x K_f = 8.314 Jmol^{-1}K^{1} -x 313^{2} K^{2} / (1000 x 7.3818 K mol^{-1}g) = 110.24 J / g = 110.34J.g^{-1}

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9. Water boils at 373K at one atmospheric pressure. At what temperature will it boil when atmospheric pressure becomes 528 mm of Hg at some space station? Latent heat of water 2.28 kJ g^{-1}(R = 8.314 JK^{-1} mol^{-1})

ln(P2/P1) = ΔH_v / R [1 /T1 – 1 /T_2] where ΔH_v = 2.28 kJ g^{-1}= 2280 x18 J mole^{-1} = 41040 J mole^{-1}

or, ln(528/760) = (41040/8.314) K^{-1} [1 / 373 – 1 /T_2]

or, -0.3642 = 4936.25 K^{-1}[1 / 373 – 1 /T_2]

or, 1 / 373 – 1 /T2 = -7.378 x 10^{-5} K^{-1}

or, 1 /T_2 = [1 / 373 +7.378 x 10^{-5}] K^{-1}

or, 1 /T_2 = 2.7547 x 10 $^{-3}$ K^{-1}

or, T_2 = 363 K

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10. The vapour pressure of n-butyl alcohol is given by the equation:

$\log_{10} P(\text{mm}) = - 2443 / T + 9.136$

Calculate the heat of vaporization per mole of the liquid at the normal boiling point, 117 °C.

As per Clausius – Clapeyron equation, $dP / dT = \Delta H_v / T (V_g-V_L)$ …………(1)

We have $\log_{10} P(\text{mm}) = - 2443 / T + 9.136$

Differentiating w. r. t. temperature T, we get,

$1/P. dP / dT = 2443/ T^2$

Or, $dP /P = 2443 dT / T^2$

Or, $\ln P = -2443/T + \text{Constant}$

Or, $\log_{10} P = -2443/2.303T + \text{Constant}$

From equation (1), $dP / dT = \Delta H_v / T (V_g-V_L) = \sim \Delta H_v / T. V_g = \Delta H_v.P/ RT^2$

Or, $dP /P = \Delta H_v. / RT^2$

Or, $\log_{10} P = - \Delta H_v /2.303 RT + \text{Constant}$ ………..(3)

Comparing equation (3) with the given equation, we get,

$- \Delta H_v /2.303R = -2443$

Or, **$\Delta H_v = 2443 \times 2.303 \times 8.314 = 46776 \text{ J K}^{-1} \text{ mol}^{-1} = 46.776 \text{ kJ K}^{-1} \text{ mol}^{-1}$**

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11. Calculate the rate of change of transition temperature with pressure of Sulphur if transition temperature is 95.5 °C at 1atm pressure, enthalpy of transition per gram of Sulphur is 13.41 J and monoclinic Sulphur (stable above transition points) has a greater specific volume than that of rhombic sulphur by 0.0126 cm3.g^{-1}.

$dP / dT = \Delta H_v / T \Delta V$

$dT / dP = T \Delta V/\Delta H_v = 368.5 \text{ K} \times 0.0126 \text{ cm}^3. \text{ g}^{-1} / 13.41 \text{ J g}^{-1} = 0.34624 \text{ K. cm}^3/\text{J}$

$= 0.34624 \text{ K. cm}^3/ 9.8628 \text{ atm cm}^3 = 0.0351 \text{K atm}^{-1}$.

∴ Rate of change of transition temperature with pressure of Sulphur temperature = 0.0351K atm^{-1}.

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12. The Henry's law constant for a solution of acetone in chloroform is 150 torr when the solution is at 308K. Calculate the value of vapour pressure of acetone when it's mole fraction is 0.14.

According to Henry's law: $P = x_B. K_H$; where K_H = Henry's constant

∙: P = 0.14 x 150 torr = 21 torr

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13. The solubility of O_2 in water at NTP is 0.0632 g per litre. At what pressure one litre of water at 0 ℃ dissolves 4.0 g of oxygen?

x_{O2} = (0.0632 /32)/ (0.0632 /32 + 1000/18) = 1.975 x 10^{-3}/55.5575 = 3.55 x 10^{-5}

K_H = P / x_{O2} = 1 atm / 3.55 x 10^{-5} = 2.813 x 10^4 atm.

P new = (4/32) / (4/32 + 1000/18) x 2.813 x 10^4 atm. = 0.125 / 55.6805 = 63.15 atm.

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14. The total vapour pressure of 4 % (mole/molecule) solution of NH_3 in water is 50 torr, the vapour pressure of pure water is 17.0 torr at this temperature. Applying Henry's law and Raoult's law, calculate the two partial pressures and total pressure for 5 % solution.

P total = p_{NH3} + p_{H2O}

x_{NH3} = 0.04; x_{H2O} = 0.96

p_{H2O} = x_{H2O} . P° = 0.96 x 17.0 torr = 16.32 torr

p_{NH3} = P total - p_{H2O} = 50 torr -16.32 torr = 33.68 torr

From Henry's law, p_{NH3} = K_H. x $_{NH3}$

Or, 33.68 torr = K_H x 0.04;

K_H = 33.68 torr/ 0.04= 842 torr

By problem, p\`$_{NH3}$ = $K_H$. x\`$_{NH3}$ = 842 torr x 0.05 = 42.1 torr

p\`$_{H2O}$ = 0.95 x 17.0 torr = 16.15 torr

Therefore, total new pressure = (16.15+ 42.1) torr = 58.25 torr

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Short Question and Answers

Q1. What is the maximum no. of phases that co-exist for a component system?

F = C-P+2 = 2-P+2 = 4-P. For P =4, F = 0
When P is maximum, then F is minimum i.e. F = 0

Q2. For a substance having three phases (solid, liquid, vapour) are in equilibrium at the triple point is invariant whereas the freezing pt. is variable. How would you account for this?

For the triple point, F = C-P+2 = 1-3+2 = 0 i.e. the system is invariant. When we consider the freezing point, we will consider it under atmospheric pressure, and it has been observed that presence of air exists over the solid or liquid. Thus, the gaseous phase contains not only water vapour but also contains air. Thus, the number of components becomes more than one and hence degree of freedom i.e. F will not be zero. Hence the freezing point is variable.

Q3. Density of monoclinic Sulphur is less than that of rhombic Sulphur – explain with the phase diagram.

In the phase diagram of Sulphur, slope of the curve is explained by the Clapeyron equation i.e. dP/dT =
L_t / T (V_m - V_r); where L_t = latent heat of transition, V_m = volume of monoclinic Sulphur and V_r = volume of rhombic Sulphur. As $V_m > V_r$, so dP/dT becomes positive. Though monoclinic and rhombic variety of Sulphur have same molecular weight, hence density of monoclinic Sulphur is less than that of rhombic Sulphur.

Q4. "A mixture of salt and ice acts as a freezing mixture". Or "Salt is spread over ice for its melting" – explain.

When salt is added into ice or when salt spreads over ice, then the ice mixture becomes three component system and applying phase rule, we get, F = C-P+2. At constant P, it becomes F = C-P+1. So, for the ice mixture, F = 2-3+1 = 0. So, the system is non variant and any variation of the variable will cause the disappearance of phase. Now a portion of the added salt dissolves in water and it causes the variation in composition. The easiest way is the disappearance of salt by getting dissolved in water. But for this type of dissolution of salt in water, it takes latent heat from the surroundings and hence surrounding temperature also falls. Due to this lowering of temperature, a mixture of salt and ice acts as a freezing mixture.

Q5. "A mixture of Na_2CO_3 and K_2CO_3 is used as fusion mixture" – explain.

Both Na_2CO_3 and K_2CO_3 are high melting solids and in the laboratory, Bunsen burner cannot provide such high temperature for melting the above compounds individually. But the mixture of both produces the solid solution having low melting point which is easily achievable in the laboratory with the help of Bunsen burner. Hence the mixture of Na_2CO_3 and K_2CO_3 is used as fusion mixture.

Q6. Why **extraction of aluminum from Al_2O_3 needs fluorspar and cryolite**?

Q7. "A mixture of Sn and Pb is used for soldering" – explain?

A mixture Sn and Pb produces a simple eutectic system having very low melting point solidifies with appreciable plasticity. This is why a mixture of Sn and Pb is suitable for soldering purpose in the electrical line.

Q8. Why ethyl alcohol and water cannot be separated into pure compounds by fractional distillation?

Ethyl alcohol and water cannot be separated into pure compounds by fractional distillation as they form azeotropic mixture having same composition at the vapour phase and in the liquid mixture.

Q9. Equimolar solutions may not be isotonic – justify your answer.

Equimolar solutions of non-electrolytes are isotonic but in the case of solutions
of electrolytes, they are not isotonic as Van't Hoff factors (i) are different.

Q10. Is it possible to have quadruple point on a phase diagram for a one-component system?

$F = C - P + 2 = 1 - P + 2 = 3 - P$

For a quadruple point, $P = 4$, then $F = 3 - 4 = -1$ which is ridiculous. Hence it is not possible to have quadruple point on a phase diagram for a one-component system.

Q11. Calculate the number of components, number of phases and degrees of freedom of the following
system: (i) A liquid at its critical temperature (ii) A binary azeotrope.

Ans:

(i) $F = C - P + 2 = 1 - 2 + 2 - 1 = 0$

(ii) $C = S - R - Z$, where where C = Number of components,

S = Number of chemical species present in the system, R = Number of independent chemical reactions and

Z = Number of restricting conditions. Therefore, $C = 3-1-0 = 1$, $F = 2 - 2 + 2 - 1 = 1$

Q12. Discuss the effect of the use of D_2O in place of water in phenol -water system in determining CST?

Ans:

In a partially miscible system, where water is one of the components, then CST changes by changing the isotopic ratio hydrogen in water e.g., in the phenol-water system, the CST is raised by using D_2O in place of water.

Problems based on Phase Rule:

Number of components for a non – reactive system = Number of constituents.
Number of components for a reactive system C = S – R - Z; where C = Number of components,
S = Number of chemical species present in the system, R = Number of independent chemical reactions,
Z = Number of restricting conditions.

I.

Calculate the number of components and degrees of freedom for the following equilibria:

(i)An aqueous solution of glucose. (ii) An aqueous solution of NaCl. (iii) An aueous solution of mixture of NaCl and KBr in equilibrium with the vapour phase. (iv) $NH_4Cl \rightleftharpoons NH_3(g) + HCl(g)$ system in which
(a) $P_{NH3} = P_{HCl}$; (b) $P_{NH3} \neq P_{HCl}$

Ans: (i) F = C -P + 2 = 2 – 1 + 2 = 3 (Temperature, Pressure and Concentration of solution)

(ii) F = 2 – 1 + 2 = 3 (T, P and concentration of solution)

(iii)

F = C - P + 2

Here C = S – R - Z where C = Number of components, S = Number of chemical species present in the system, R = Number of independent chemical reactions, Z = Number of restricting conditions.
Thus C =10 – 5 - 1 = 4
∴ F = 4 – 1 + 2 = 5

(iv)

(a) F = C - P + 2
Here C = S – R - Z where C = Number of components, S = Number of chemical species present in the system, R = Number of independent chemical reactions, Z = Number of restricting conditions.
∴C = 3 - 1 – 1 = 1

∴ F = 1 – 2 + 2 = 1

(b)

F = C - P + 2
Here C = S – R - Z where C = Number of components, S = Number of chemical species present in the system, R = Number of independent chemical reactions, Z = Number of restricting conditions.
∴ C = 3 - 1 – 0 = 2

∴ F = 2 – 2 + 2 =2

II.
Calculate the number of components, phases and degrees of freedom in the following equilibrium:

$$CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g) \text{ in a sealed tube}$$

Ans:
F = C - P + 2
Here C = S – R - Z where C = Number of components, S = Number of chemical species present in the system, R = Number of independent chemical reactions, Z = Number of restricting conditions.

∴ C = S – R – 0 = 3-1 - 0 = 2
F = C – P + 2 =2 – 3 (2 solid +1 gas) +2 = 1

III.
Write down the number of components, number of phases and degrees of freedom for the following equilibria:

(i) $N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2\ NH_3\ (g)$

(ii) $Fe\ (s) + H_2O\ (g) \rightleftharpoons FeO\ (s) + H_2\ (g)$

(iii) $H_2O\ (g) \rightleftharpoons H_2\ (g) + \frac{1}{2}\ O_2\ (g)$

Ans:

(i) $N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2\ NH_3\ (g)$

For this type of reaction C = S – R + Z; Here S = 3, R =1, Z = 0
·: C = 3 – 1 – 0 = 2
P = 1; F = C – P + 2 = 2 - 1 +2 = 3

(ii) $Fe\ (s) + H_2O\ (g) \rightleftharpoons FeO\ (s) + H_2\ (g)$

For this type of reaction C = S – R + Z; Here S = 4, R =1, Z = 0;
C = 4 – 1 + 0 = 3
F = 3 – 3 + 2 = 2

(iii) $H_2O\ (g) \rightleftharpoons H_2\ (g) + \frac{1}{2}\ O_2\ (g)$

For this type of reaction C = S – R - Z; Here S = 3, R =1, Z = 1;
C = 3 – 1 – 1 = 1
F = 1 – 1 + 2 = 2

IV.

Calculate the number of components and the degrees of freedom in

(i) An aqueous solution of acetic acid
(ii) Pure partly frozen acetic acid
(iii) A dilute solution of sulphuric acid in water

Ans:

(i) C = S – R + Z; here C = 2 – 0 -0 = 2; F = 2 – 1 +2 = 3
(ii) C = S – R + Z; here C = 1- 0 – 0 = 1; F = 1 – 2 + 2 = 1
(iii)C = S – R + Z; a dilute solution of sulphuric acid in water gives itself H_2SO_4, H_2O, H_3O^+,
HSO_4^-, SO_4^{-2}. Therefore, S = 5, R = 2 and Z = 1
·: C = 5 – 2 - 1 = 2; F = 2 – 1 + 2 = 3

V.

Write down the number of components, number of phases and degrees of freedom for the followings:

(i) $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$
(ii) Solid carbon in equilibrium with gases CO (g), CO_2 (g) and O_2 (g) at 373 K.
(iii) NH_4Cl (s) partially dissociated into $NH_3(g) + HCl(g)$

Ans:

(i) C = S – R – Z = 2 -1 -0 =1; F = 1 – 1 +2 = 2
(ii) C = S – R – Z = 4 - 2 – 1 = 1; F = 1 – 2 + 2 = 1
(iii) C = S – R – Z = 3 – 1- 0 = 2; F = 2 – 2 + 2 = 2