

Solutions to Problem Set 8

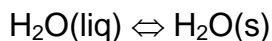
1. water saturated with H₂ and O₂ gases at a total pressure of 5 atm with (2:1 = H₂:O₂)

Equation	Basis for the equation	Eq. #
5 atm = p _{H2} +p _{O2} ; p _{H2} /p _{O2} = 2/1	Given	1
p _{H2} = (2/3) 5 atm = 3.333 atm p _{O2} = (1/3) 5 atm = 1.666 atm		
p _{H2} = K _H (H ₂) x _{H2}	Henry's law applied to H ₂ gas solubility Concentration in solution is directly proportional to the partial pressure of the gas above the solution	2
3.333 atm = 7.76 × 10 ⁴ atm x _{H2} x _{H2} = 3.333/7.76×10 ⁴ = 4.295×10 ⁻⁵	p _{H2} = partial pressure of H ₂ in the overhead gas x _{H2} = mole fraction of H ₂ in the aqueous solution	3
p _{O2} = K _H (O ₂) x _{O2} 1.666 atm = 4.58 × 10 ⁴ atm x _{O2} x _{O2} = 1.666/4.58×10 ⁴ = 3.639×10 ⁻⁵	K _H (in atm) is given in provided table Solubility of these gases do not strictly follow Henry's law, since the apparent Henry's law constant from experiment varies with overhead partial pressure! Use the K _H at the closest partial pressure (as we have done here). Better yet, make a least squares fitting of apparent K _H vs p and use the equation to find the appropriate K _H to use at the partial pressures of this problem.	4
mole ratio of H ₂ :O ₂ in solution was 4.295×10 ⁻⁵ /3.639×10 ⁻⁵ = 1.18 or 54.1 mole% H ₂ 45.9 mole% O ₂ in the gases driven off Answer		

2. vapor pressure lowering by a solute

Equation	Basis for the equation	Eq. #
p _{Bz} / p* _{Bz} = x _{Bz} 74.01/74.66 = x _{Bz} = 0.9913	Assuming ideal solution for the solvent, Raoult's law holds	1
100 g C ₆ H ₆ /78 g mol ⁻¹ = 1.282 mol Bz		2
1.282/[1.282 mol + n] = 0.9913 n = 0.01125 mol solute	Find n number of moles of solute in 100 g Bz	3
2 g/MW g mol ⁻¹ = 0.01125	Find molecular weight of solute	4
MW = 178		5
178 = c 12 + h 1	For molecular formula C _c H _h	6
c 12/178 = 0.944		
c = 14		
178 = 14(12) + h(1)	weight fraction of carbon in this formula is 94.4% Solve for c	7
h = 10	Substitute c into Eq 6	8
The molecular formula is C ₁₄ H ₁₀ Answer		

3. Freezing point depression by a solute



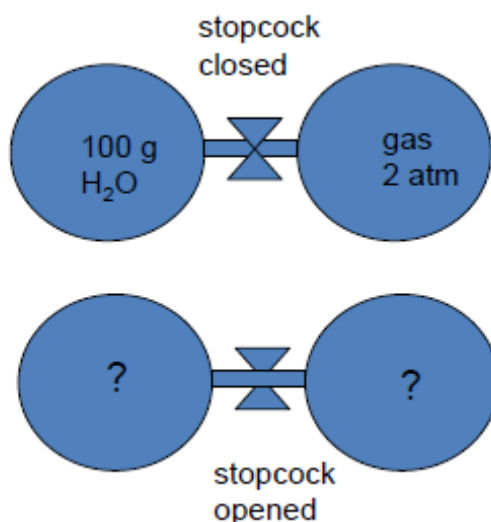
Equation	Basis for the equation	Eq. #
$\mu^*_{\text{H}_2\text{O},\text{liquid}}(\text{T},\text{p}^*) = \mu^*_{\text{H}_2\text{O},\text{vap}}(\text{T},\text{p}^*)$	Pure liquid H_2O in equilibrium with its vapor, * means pure	1
$\mu^*_{\text{H}_2\text{O},\text{vap}}(\text{T},\text{p}^*) = \mu^{\ominus}_{\text{H}_2\text{O},\text{vap}}(\text{T}) + RT \ln(\text{p}^*/1\text{atm})$	For the vapor at a given temperature, behaving like an ideal gas Recall that we used $d\mathbf{G} = Vdp$ when $dT = 0$ and replaced V by RT/p to get this. If non-ideal vapor use $RT \ln(f/1\text{atm})$ instead	2
$\mu_{\text{H}_2\text{O},\text{liquid solution}}(\text{T},\text{p}) = \mu_{\text{H}_2\text{O},\text{vap}}(\text{T},\text{p})$ $\mu_{\text{H}_2\text{O},\text{vap}}(\text{T},\text{p}) = \mu^{\ominus}_{\text{H}_2\text{O},\text{vap}}(\text{T}) + RT \ln(\text{p}_{\text{H}_2\text{O}}/1\text{atm})$	H_2O in aqueous solution in equilibrium with its vapor. As above, except that partial pressure $\text{p}_{\text{H}_2\text{O}}$ of H_2O in the vapor in equilibrium with liquid solution is less than p^*	3 4
$\mu_{\text{H}_2\text{O},\text{liquid solution}}(\text{T},\text{p}) - \mu^*_{\text{H}_2\text{O},\text{liquid}}(\text{T},\text{p}^*) = RT \ln(\text{p}_{\text{H}_2\text{O}}/\text{p}^*)$	Eq. (3+4) minus Eq (1+2)	5
$\text{p}_{\text{H}_2\text{O}}/\text{p}^* = x_{\text{H}_2\text{O}}$	Assume Raoult's law holds for the liquid solution	6
$\mu_{\text{H}_2\text{O},\text{liquid solution}}(\text{T},\text{p}) - \mu^*_{\text{H}_2\text{O},\text{liquid}}(\text{T},\text{p}^*) = RT \ln x_{\text{H}_2\text{O}}$	Substituting Eq 6 into Eq 5	7
For $\text{H}_2\text{O}(\text{liq}) \rightleftharpoons \text{H}_2\text{O}(\text{s})$ at equilibrium at T^*_f and 1 atm, $\mu^*_{\text{H}_2\text{O},\text{solid}}(\text{T}^*_f, 1 \text{ atm}) = \mu^*_{\text{H}_2\text{O},\text{liquid}}(\text{T}^*_f, 1 \text{ atm})$	Pure liquid water in equilibrium with ice at the normal freezing point T^*_f	8
For $\text{H}_2\text{O}(\text{liq solution}) \rightleftharpoons \text{H}_2\text{O}(\text{s})$ at equilibrium at T and 1 atm, $\mu^*_{\text{H}_2\text{O},\text{solid}}(\text{T}, 1 \text{ atm}) = \mu_{\text{H}_2\text{O},\text{liquid solution}}(\text{T}, 1 \text{ atm})$	Aqueous solution in equilibrium with pure ice at the new freezing point T	9
$\mu^*_{\text{H}_2\text{O},\text{solid}}(\text{T}, \text{p}) = \mu^*_{\text{H}_2\text{O},\text{liquid}}(\text{T},\text{p}) + RT \ln x_{\text{H}_2\text{O}}$	Applying Eq 10 and Eq 7	10
$\ln x_{\text{H}_2\text{O}} = [\mu^*_{\text{H}_2\text{O},\text{solid}}(\text{T}, \text{p}) - \mu^*_{\text{H}_2\text{O},\text{liquid}}(\text{T},\text{p})]/RT$	Rearrange Eq 11	11
$\ln x_{\text{H}_2\text{O}} = - [\Delta_{\text{fus}}\mathbf{G}]/RT$		12
$(\partial \ln x_{\text{H}_2\text{O}} / \partial x_{\text{H}_2\text{O}}) = - (1/R) \bullet [\partial (\Delta_{\text{fus}}\mathbf{G}/T) / \partial T]_p \bullet (\partial T / \partial x_{\text{H}_2\text{O}})_p$	To discover how new freezing point T depends on the water concentration in the liquid solution $x_{\text{H}_2\text{O}}$, p being constant, we need to evaluate $(\partial T / \partial x_{\text{H}_2\text{O}})_p$ Apply $(\partial / \partial x_{\text{H}_2\text{O}})$ to Eq 13	13
$[\partial (\Delta_{\text{fus}}\mathbf{G}/T) / \partial T]_p = - \Delta_{\text{fus}}\mathbf{H}/T^2$	Gibbs-Helmholtz equation which we derived previously	14
$(\partial \ln x_{\text{H}_2\text{O}} / \partial x_{\text{H}_2\text{O}}) = [\Delta_{\text{fus}}\mathbf{H}/RT^2] \bullet (\partial T / \partial x_{\text{H}_2\text{O}})_p$	Substitute Eq 15 into Eq 14	15

$1/x_{\text{H}_2\text{O}} = [\Delta_{\text{fus}}\mathbf{H}/RT^2] \bullet (\partial T/\partial x_{\text{H}_2\text{O}})_p$		16
$dx_{\text{H}_2\text{O}}/x_{\text{H}_2\text{O}} = (\Delta_{\text{fus}}\mathbf{H}/R) dT/T^2$		17
$\int dx_{\text{H}_2\text{O}}/x_{\text{H}_2\text{O}} = \int (\Delta_{\text{fus}}\mathbf{H}/R) dT/T^2$	Integrating	18
$\int_1^{x_{\text{H}_2\text{O}}} dx_{\text{H}_2\text{O}}/x_{\text{H}_2\text{O}} = \int_{T_f^*}^T (\Delta_{\text{fus}}\mathbf{H}/R) dT/T^2$	Between the limits of 1 mole fraction (pure liquid water) and $x_{\text{H}_2\text{O}}$, and corresponding temperatures T_f^* and new freezing temperature T .	19
$\ln x_{\text{H}_2\text{O}} = (\Delta_{\text{fus}}\mathbf{H}/R) \{ -T^{-1} + T_f^{*-1} \}$	Assume $\Delta_{\text{fus}}\mathbf{H} = 80 \text{ cal g}^{-1}$ and is only mildly dependent on T over this tiny temperature range	20
$\ln x_{\text{H}_2\text{O}} = (80/1.9872) \{ -263^{-1} + 273^{-1} \}$ $= -0.00561$ $x_{\text{H}_2\text{O}} = 0.9944$	For $T = 263 \text{ K}$	21
$n_{\text{H}_2\text{O}} = 4000/18 = 222.22$ $x_{\text{H}_2\text{O}} = n_{\text{H}_2\text{O}}/(n_{\text{H}_2\text{O}} + n_{\text{solute}})$ $0.9944 = 222.22/(222.22 + n_{\text{solute}})$ $n_{\text{solute}} = 1.25 \text{ mol}$	Using density of water = 1 g mL^{-1} , given 4 L H_2O weighs 4000 g	22
$\text{g CH}_3\text{OH} = 1.25(32) = 40$ $\text{g C}_2\text{H}_4(\text{OH})_2 = 1.25(62) = 77.5$ Answers	Weights of methanol and ethylene glycol to be dissolved in 4 L water to prevent ice formation at 263 K	23

4. Freezing point depression by a solute and osmotic pressure

Equation	Basis for the equation	Eq. #
$\ln x_{\text{H}_2\text{O}} = (\Delta_{\text{fus}}\mathbf{H}/R) \{ -T^{-1} + T_f^{*-1} \}$	Following same derivation as in problem 3 above	1
$\ln x_{\text{H}_2\text{O}} = (80/1.9872) \{ -272.74^{-1} + 273^{-1} \}$ $= -2.016 \times 10^{-4}$	Substituting $\Delta_{\text{fus}}\mathbf{H} = 80 \text{ cal g}^{-1}$ and $T_f^* = 273.15$ for water and given $t = -0.406^\circ\text{C} = 272.74 \text{ K}$	2
$V\pi = -RT \ln x_{\text{H}_2\text{O}}$	following derivation in Problem Set 7 prob. 1(b)	3
$V\pi = -RT(-2.016 \times 10^{-4})$	Substituting Eq 2 into Eq 3	4
$\pi = - (8.31451 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}) 298$ $\bullet (-2.016 \times 10^{-4}) / 18 \times 10^{-6} \text{ m}^3$ $\pi = 27750 \text{ Pa}$ Answer	Using the molar volume of water = $18 \times 10^{-6} \text{ m}^3$ based on molar mass of 18g, density of 1 g cm^{-3} at 298 K. This answer is inaccurate because we assumed that NaCl is undissociated in solution and the solution is an ideal solution. To do the problem correctly, we will need to use activities of the + and - ions in the solution, all of which contribute to the osmotic pressure. We will find out more about ionic activities in Lecture notes part 9.	5
Alternatively, we also could have done this. $\ln x_{\text{H}_2\text{O}} = \ln(1-x_s) \approx -x_s - (1/2)x_s^2 - (1/3)x_s^3 - \dots$	Use the sum of mole fractions = 1 and expand the \ln in a series	4a
$V\pi = RT x_s$	The relation between molar volume of liquid water the osmotic pressure and the mole fraction of salt	5a

5.



10 L bulbs, $T = 298\text{ K}$ throughout

Vapor pressure of water = 24 mm Hg = 0.0316 atm

solubility of gas in water is 2 moles per 1000 g water

Equation	Basis for the equation	Eq. #
$2\text{ atm} \cdot 10\text{ L} =$ $n_{\text{gas}} (0.0820578\text{ L atm K}^{-1}\text{ mol}^{-1}) 298\text{ K}$ $n_{\text{gas}} = 0.818\text{ mol}$	<i>Initially</i> with stopcock closed, the left bulb has water and water vapor. Volume of liquid water is very close to 100 mL. Available volume for water vapor is $(10. - 0.100) = 19.90\text{ L}$. If behaving as an ideal gas Right bulb only has 0.818 mol gas in the 10 L volume.	1
	<i>At equilibrium after stopcock is opened</i> , some gas goes into the left bulb into solution, liquid water remains in the left bulb and the gas phase now occupies a total of 19.90 L containing water vapor plus gas	1
mol of gas that went into 100 g liquid water is 0.20 mol Gas phase therefore has $0.818 - 0.20 = 0.618\text{ mol}$ gas in 19.90 L plus that amount of water vapor that corresponds to a partial pressure of 0.0316 atm and 19.90 L	First assume amount of liquid water that has turned into water vapor is much much less than 100 g. then later test whether this is true or not. Using the given gas solubility	1

$0.0316 \text{ atm} \cdot 19.90 \text{ L}$ $= n (0.0820578 \text{ L atm K}^{-1} \text{ mol}^{-1}) 298 \text{ K}$ $n_{\text{water vapor}} = 0.0257 \text{ mol}$ $\text{g water vapor} = 0.0257 \text{ mol} (18 \text{ g mol}^{-1})$ $= 0.46 \text{ g}$	<p>Assuming water vapor behaves as an ideal gas</p> <p>The mass of liquid water that this corresponds to is 0.46 g, occupying a volume of 0.46 mL So our assumption that the amount of liquid water that has turned into water vapor is much, much less than 100 g is quite good since $0.46 \ll 100.0$. Also, the volume available to the gas phase is 19.90046, that is, 19.90 is therefore close enough.</p>	1
<p>In summary, equilibrium condition has 99.54 g of liquid water in the left bulb, and in the gas phase spread into both bulbs are 0.0257 mol water vapor and 0.618 mol of the gas. The partial pressure of the gas is</p> $0.618 \text{ mol} (0.0820578 \text{ L atm K}^{-1} \text{ mol}^{-1}) 298 \text{ K} / 19.9 \text{ L} = 0.759 \text{ atm}$ <p>The total pressure in the gas phase is therefore $0.759 + 0.0316 = 0.791 \text{ atm}$</p> <p style="text-align: center;">Answer</p>		2

6. At 40°C 1 g of CO₂ will dissolve under 1 atm pressure in 1000 g H₂O.

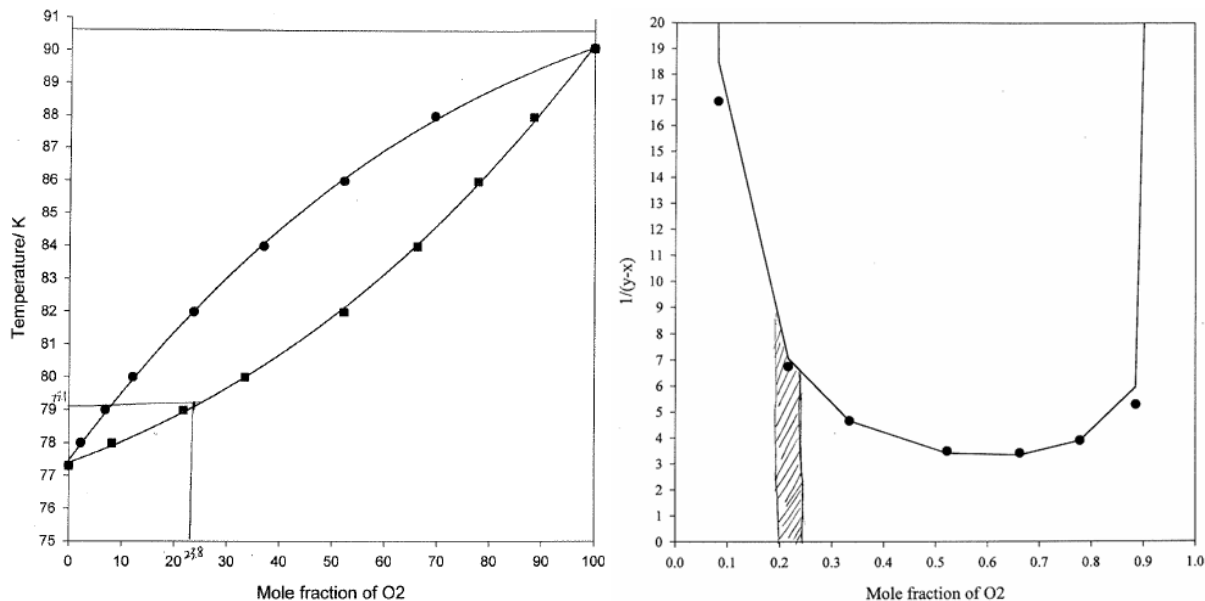
At 20°C 1.7 g of CO₂ will dissolve under 1 atm pressure in 1000 g H₂O.

Equation	Basis for the equation	Eq. #
<p>At 40°C 1 g of CO₂ will dissolve under 1 atm pressure in 1000 g H₂O.</p> <p>At 40°C 2 g of CO₂ will dissolve under 2 atm pressure in 1000 g H₂O.</p>	<p>Given</p> <p>We are allowed to assume Henry's law holds $p_{\text{CO}_2} = K_{\text{H}}(\text{CO}_2) x_{\text{CO}_2}$ at 40°C</p>	1
<p>Thus, we must have no more than 2 g of CO₂ in 1000 g H₂O at 20°C</p> <p>At 20°C 1.7 g of CO₂ will dissolve under 1 atm pressure in 1000 g H₂O. this corresponds to a pressure of $(2/1.7) = 1.176 \text{ atm}$ of CO₂ at 20°C</p> <p style="text-align: center;">Answer</p>	<p>Using the given 2 atm pressure for the bursting limit (and we are neglecting the vapor pressure of water so that total pressure is entirely due to CO₂)</p> <p>Given</p> <p>Using $p_{\text{CO}_2} = K_{\text{H}}(\text{CO}_2) x_{\text{CO}_2}$ at 20°C</p>	2
<p>1.7 g is $1.7/44 = 0.0386 \text{ mol CO}_2$</p> <p>1000 g is $1000/18 = 55.555 \text{ mol H}_2\text{O}$</p> <p>1 atm $= K_{\text{H}}(\text{CO}_2) 0.0386 / [55.555 + 0.0386]$ $= K_{\text{H}}(\text{CO}_2) 0.000695$ $K_{\text{H}}(\text{CO}_2) = 1439.3 \text{ atm}$</p>	<p>Using molar masses of CO₂ and H₂O</p> <p>Find the $K_{\text{H}}(\text{CO}_2)$ at 20°C</p> <p>Applying $p_{\text{CO}_2} = K_{\text{H}}(\text{CO}_2) x_{\text{CO}_2}$ at 20°C</p>	3

1.176 atm of CO_2 at 20°C therefore corresponds to
 $x_{\text{CO}_2} = 1.176/1439 = 0.00082$ **Answer**

Substituting the value of K_H into
 $p_{\text{CO}_2} / K_H(\text{CO}_2) = x_{\text{CO}_2}$ at 20°C

7. T vs X diagram for O_2 - N_2 mixture at 1 atm.



Let L be the amount of liquid remaining in the still at a given instant during the distillation. After distilling a differential amount dL , the amount of liquid will be $(L - dL)$ and the amount of vapor formed will be dL . At the instant, the composition of the liquid is X_{O_2} and the composition of the vapor is Y_{O_2} . Consider material balance of O_2 component: O_2 overall = O_2 in the remaining liquid + O_2 in the vapor

$$(L)(X_{\text{O}_2}) = (L - dL)(X_{\text{O}_2} - dX_{\text{O}_2}) + (dL)(Y_{\text{O}_2} + dY_{\text{O}_2})$$

Neglecting products of infinitesimals,

$$(L)(X_{\text{O}_2}) = (L)(X_{\text{O}_2}) - (X_{\text{O}_2})(dL) - (L)(dX_{\text{O}_2}) + (dL)(Y_{\text{O}_2}) \quad \text{or } (Y_{\text{O}_2} - X_{\text{O}_2})(dL) = (L)(dX_{\text{O}_2})$$

$$\frac{(dL)}{(L)} = \frac{(dX_{\text{O}_2})}{(Y_{\text{O}_2} - X_{\text{O}_2})}$$

$$(L) \quad (Y_{\text{O}_2} - X_{\text{O}_2})$$

LIQUID: the overall composition is 0.20 O_2 and 90 % is distilled, that is 10 % remaining

$$\text{Integrating, from 10\% up to 100\%, } \ln(L_2/L_1) = \ln(1.00/0.10) = 2.303 = \int_{X_{\text{O}_2}}^{0.20} \frac{(dX_{\text{O}_2})}{(Y_{\text{O}_2} - X_{\text{O}_2})}$$

from molefraction 0.20 O_2 to X_{O_2} . Plot the curve $(Y_{\text{O}_2} - X_{\text{O}_2})^{-1}$ vs X_{O_2} (see figure above right). Now find the value of X_{O_2} at which the integral underneath the curve between X_{O_2} and 0.20 is equal to 2.303.

We read $X_{\text{O}_2} = 0.23$ is the composition of the remaining liquid. **Answer**

And (reading T for which $X_{\text{O}_2} = 0.23$ in the figure above left) this occurs at $T = 79.1 \text{ K}$.

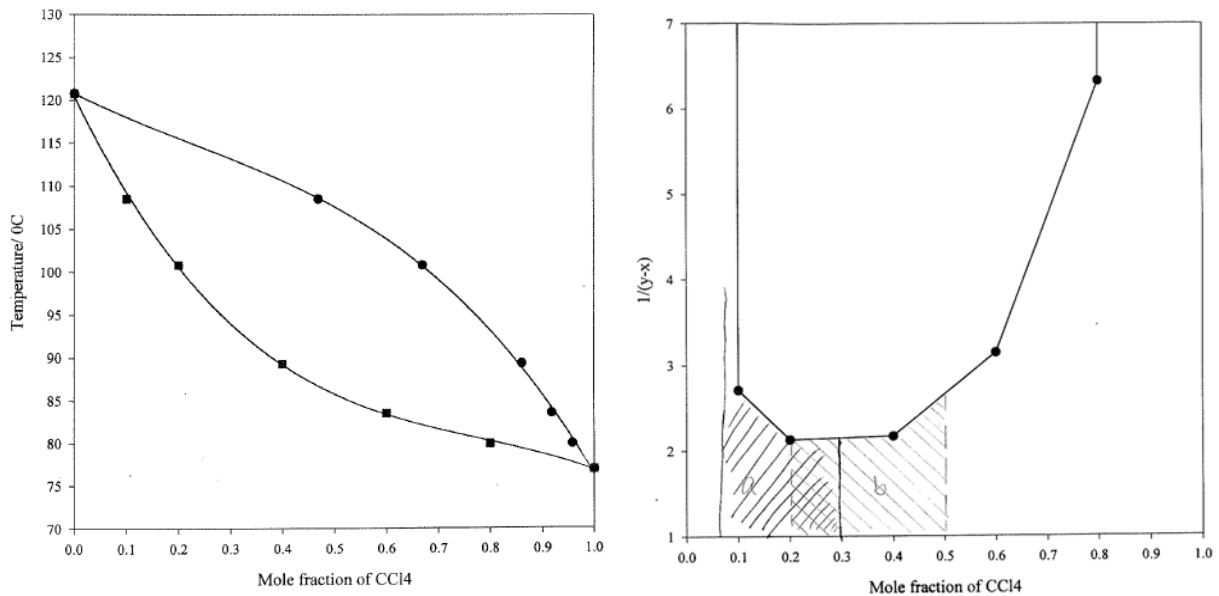
Answer

Calculate activities: $a_{\text{O}_2} = p_{\text{O}_2}/p_{\text{O}_2}^*$ $Y_{\text{O}_2} = p_{\text{O}_2}/p_{\text{tot}}$ $p_{\text{tot}} = 1.0 \text{ atm}$ $a_{\text{O}_2} = Y_{\text{O}_2} \cdot (1 \text{ atm}/p_{\text{O}_2}^*)$

We can get $p_{\text{O}_2}^*$ using the Clausius Clapeyron Eq

X_{O_2}	0.0	0.081	0.216	0.334	0.522	0.662	0.778	0.885	1.0
a_{O_2}	0	0.022	0.068	0.12	0.236	0.369	0.522	0.696	1.0
		$/p_{\text{O}_2}^*_{78\text{K}}$	$/p_{\text{O}_2}^*_{79\text{K}}$	$/p_{\text{O}_2}^*_{80\text{K}}$	$/p_{\text{O}_2}^*_{82\text{K}}$	$/p_{\text{O}_2}^*_{84\text{K}}$	$/p_{\text{O}_2}^*_{86\text{K}}$	$/p_{\text{O}_2}^*_{88\text{K}}$	

8. T vs X diagram for CCl₄ - C₂Cl₄ mixture at 1 atm.



(a) LIQUID: the overall composition is 0.30 CCl₄ and 50 % is distilled, that is 50 % remaining

Integrating, from 50% up to 100%, $\ln (L_2/L_1) = \ln (1.00/0.50) = 0.693 = \int_{0.30}^{1.00} \frac{dX}{Y - X}$

from molefraction 0.30 CCl₄ to X. Plot the curve $(Y - X)^{-1}$ vs X (see figure above right). Now find the value of X at which the integral underneath the curve between X and 0.30 (hatched area a) is equal to 0.693.

We read X = 0.044 is the CCl₄ composition of the remaining liquid. To find the Y (in the collected distillate), apply mass balance for CCl₄:

CCl₄ overall = CCl₄ in the remaining liquid + CCl₄ in the collected distillate

$0.30 L = 0.044(L/2) + Y(L/2)$; Solve for Y, Y = 0.556

Answer

(b) LIQUID: the overall composition is 0.50 CCl₄ and is distilled until remaining liquid is 0.20 CCl₄. If the distillate is removed continuously, then at the instant that the liquid is 0.20 CCl₄, the vapor coming off is 0.67 CCl₄ (as seen in the table).

Answer

On the other hand, if looking for Y composition in the total collected distillate, first find the area underneath the curve (figure above right) between X = 0.20 and X = 0.50, and

$\ln (1.00/f) = \int_{0.20}^{0.50} \frac{dX}{Y - X}$

The hatched area b provides the value of the fraction f of the liquid remaining.

We find the area = 0.93 = $\ln (1/f)$; $1/f = 2.53$; thus f = 0.395

Mass balance of CCl₄ is applied, knowing f = 0.395, to find Y the CCl₄ composition of the total collected distillate.

$0.50 L = 0.20L(0.395) + Y L(0.605)$ Solve for Y, Y = 0.70

Answer

This is larger than 0.67. Since CCl₄ is the lower boiling component, at the beginning where the liquid is 0.50 CCl₄, the first vapor to come off is about 0.90 CCl₄, and this Y value diminishes to the point where the remaining liquid is 0.20 CCl₄ the vapor coming off is 0.67 CCl₄, as we saw in the table. Therefore the total collected vapor has to have Y CCl₄ greater than 0.67

9. 1 g of antibiotic substance MW = 10000 g mol⁻¹ is dissolved in 100 g H₂O.

Equation	Basis for the equation	Eq. #
1 g is 1/10000 = 0.0001 mol substance		
100 g is 100/18 = 5.5555 mol H ₂ O		1
$x_s = 0.0001/(5.5555 + 0.0001) = 1.8 \times 10^{-5}$		
$1 - x_s = x_{H_2O}$		
$\ln x_{H_2O} = \ln(1 - x_s) \approx -x_s - (1/2)x_s^2 - (1/3)x_s^3 - \dots$	Expansion of $\ln(1 - x_s)$ for $x_s \ll 1$, as in this case	2
$\ln x_{H_2O} = -x_s$ is close enough		3
$p_A/p_A^* = x_A$	Raoult's law holds for the solution, here solvent A is H ₂ O	4
Since x_s is very small here, x_{H_2O} is very close to 1 so p_A will be quite close to p_A^* thus, this is not a practical test.		
$\ln x_A = \Delta_{fus} H/R \left[\frac{-1}{T} + \frac{1}{T^*} \right]$	freezing point depression following derivation in problem 3 above	5
$-x_s = (80/1.9872) (T - T^*)/T^{*2}$ $-1.8 \times 10^{-5} = 40.26 [- (T^* - T)/273^2]$ $(T^* - T) = 0.033 \text{ deg}$ Answer freezing point depression is small, not a very practical test		6
$\ln x_A = \Delta_{vap} H/R \left[\frac{1}{T} - \frac{1}{T^*} \right]$	boiling point elevation, by an analogous derivation	7
$-x_s = (539.43/1.9872) (T^* - T)/373^2$ $-1.8 \times 10^{-5} = 271.45 [- (T^* - T)/373^2]$ $(T - T^*) = 0.0092 \text{ deg}$ Answer boiling point elevation is very small, not a very practical test		8
$V\pi = RT x_s$	osmotic pressure following derivation in Problem Set 7 prob. 1(b) and problem 4 above	9
$\pi = RT x_s/V$ $\pi = (8.31451 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}) 298 \cdot (1.8 \times 10^{-5}) / 18 \times 10^{-6} \text{ m}^3$ $= 2477 \text{ Pa or } 18.57 \text{ mm Hg}$ Answer This is easily measurable and this is the preferred test, especially since only a few mg of substance is available for testing. Answer	Using the molar volume of water = $18 \times 10^{-6} \text{ m}^3$	10

10. vapor pressure of zinc at 773 K, $T_{\text{boil}} = 1180 \text{ K}$

Equation	Basis for the equation	Eq. #
$\ln(p/1\text{atm}) = (\Delta_{\text{vap}}H - H_{\text{liq}}) / RT_{\text{boil}} \cdot [1 - T_{\text{boil}}/T]$ If we know $\Delta_{\text{vap}}H$ at T_{boil} , we can find vapor pressure p at temperature T $\Delta_{\text{vap}}H$ for the phase change at 1180 K is 21 (1180) = 24780 cal mol ⁻¹	As we derived in Problem Set 7 prob 6 <u>when we could assume that the vapor behaved like an ideal gas.</u> (the Clausius Clapeyron equation) Since this value is not given, we estimate the value of $\Delta_{\text{vap}}H$ at T_{boil} Trouton's rule: $\Delta_{\text{vap}}H / T_{\text{boil}} \approx 21 \text{ cal mol}^{-1} \text{ K}^{-1}$	1 2
For any temperature T , we need to correct this $\Delta_{\text{vap}}H$ value by using $(\partial H / \partial T)_p dT$ integrated from 1180 K to T for both the liquid and the vapor $\Delta_{\text{vap}}H_T = \Delta_{\text{vap}}H_{1180 \text{ K}} + \int_{1180}^T [C_p(\text{vap}) - C_p(\text{liq})] dT$ $\Delta_{\text{vap}}H_T = \Delta_{\text{vap}}H_{1180 \text{ K}} + \int_{1180}^T [4.968 - 7.09 + 1.15 \times 10^{-3} T] dT$ $\Delta_{\text{vap}}H_T = \Delta_{\text{vap}}H_{1180 \text{ K}} + 2.122(T - 1180) + 1.15 \times 10^{-3} (1/2)[T^2 - 1180^2]$ $\Delta_{\text{vap}}H_{773} = \Delta_{\text{vap}}H_{1180 \text{ K}} - 2.122(773 - 1180) + 0.000575 [773^2 - 1180^2]$ $= \Delta_{\text{vap}}H_{1180 \text{ K}} + 863.6 - 457.0$ $= \Delta_{\text{vap}}H_{1180 \text{ K}} + 406.5$ $\Delta_{\text{vap}}H_{773} = 24780 + 406.5 = 25186$ As expected, $\Delta_{\text{vap}}H$ is higher at the lower temperature. Our answer would be in error if we had assumed $\Delta_{\text{vap}}H$ is independent of T	Here we are allowed to assume that $C_p(\text{vap}) = (5/2)R = 4.968 \text{ cal mol}^{-1}$ and we are given $C_p(\text{liq}) = 7.09 - 1.15 \times 10^{-3} T$ in cal mol ⁻¹	3
$\ln(p/1\text{atm}) = (\Delta_{\text{vap}}H_{773} / R) \cdot [1 - (1180/773)] / 1180$ $\ln(p/1\text{atm}) = 12672 \cdot -4.46 \times 10^{-4} = -5.65$ $p/1 \text{ atm} = \exp(-5.65) = 0.00352$ Answer On the other hand, if we used $\Delta_{\text{vap}}H_{1180 \text{ K}} = 24780$ $\ln(p/1\text{atm}) = 12468 \cdot -4.46 \times 10^{-4} = -5.56$ $p/1 \text{ atm} = \exp(-5.56) = 0.00385$ The vapor pressure would be 9% too high if we assume that $\Delta_{\text{vap}}H$ is independent of T Answer	Using Eq 1 (the Clausius Clapeyron equation) Actually our largest error is in assuming that Trouton's rule holds.	4