Exam II CHM 3410, Dr. Mebel, Fall 2013 (Each problem is 20 pts.)

1. Carbon tetrachloride melts at 250 K. The vapor pressure of the liquid is 10539 Pa at 290 K and 74518 Pa at 340 K. The vapor pressure of the solid is 270 Pa at 232 K and 1092 Pa at 250 K.

- (a) Calculate $\Delta H_{\text{vaporization}}$ and $\Delta H_{\text{sublimation}}$.
- (b) Calculate ΔH_{fusion} .
- (c) Calculate the normal boiling point and $\Delta S_{\text{vaporization}}$ at the boiling point.

2. The average human with a body weight of 70 kg has a blood volume of 5.00 L. The Henry's law constant for the solubility of N_2 in water is 9.04×10^4 bar at 298 K. Assume that this is also the value of the Henry's law constant for blood and that the density of blood is 1.00 kg L⁻¹.

- (a) Calculate the number of moles of N₂ absorbed in this amount of blood in air of composition of 80% N₂ at sea level, where the pressure is 1 bar, and at a pressure of 50 bar.
- (b) Assume that a diver was breathing compressed air at a pressure of 50 bar and then was suddenly brought to the sea level. What volume of N₂ gas was released as bubbles in the diver's bloodstream?

3. A sample of glucose (C₆H₁₂O₆) of mass 4.55 g is placed in a test tube of radius r = 2.50 cm. The bottom of the test tube is a membrane that is semipermeable to water. The tube is partially immersed in a beaker of water at 298 K so that the bottom is only slightly below the level of the water in the beaker. The density of water at this temperature is 997 kg m⁻³. After equilibrium is reached, how high is the water level of the water in the tube above that in the beaker. What is the value of the osmotic pressure? Assume that the test tube is cylindrical and the volume of the solution in the tube can be calculated as $V = \pi r^2 h$ and that the density of the solution in the tube is equal (approximately) to the density of water.

4. The phase diagram for two metals A and B contains one eutectic and no compound between A and B forms. The freezing points of solutions of A and B are found to vary linearly with the mole fraction of B in the solution. The melting points of pure A and B are 650 K and 600 K, respectively. The cooling curve for a mixture containing 40% mole fraction of B exhibits a single flat region (eutectic halt) at 400 K. Using this information, sketch the A-B phase diagram and indicate the phases present in each region.
5. Describe how Le Chatelier's principle is manifested in changes of equilibrium constant (or equilibrium composition of a reaction mixture) with temperature and pressure.
Support your explanation with formal equations showing the described changes.

Exam II CHM 3410, Dr. Mebel, Fall 2014 (Each problem is 20 pts.)

1. For water, $\Delta H_{\text{vaporization}}$ is 40.656 kJ mol⁻¹, and the normal boiling point is 373.12 K. Calculate the boiling point for water on the top of Mt. Rainier (elevation 4392 m), where the barometric pressure is 461 Torr.

2. At 39°C, a solution of ethanol ($x_A = 0.9006$, $p_A^* = 130.4$ Torr) and isooctane ($p_B^* = 43.9$ Torr) forms a vapor phase with the mole fraction of ethanol $y_A = 0.6667$ at a total pressure of 185.9 Torr.

- (a) Calculate the activity and activity coefficient for each component.
- (b) Calculate the total pressure that the solution would have if it were ideal.

3. 3 g of a nonvolatile solute whose molar mass is 344.2 g mol^{-1} are dissolved in 1 kg of H₂O at 298.15 K. The solution is placed in an osmotic pressure apparatus with semipermeable membrane that permits the flow of H₂O, but not the solute, between compartments. Compute the osmotic pressure of this solution. How high will be the liquid in the column when the equilibrium is established?

4. Please, see below the liquid-vapor phase diagram of the acetone/chloroform mixture at p = 1 atm. Mark each area of the phase diagram with the number of phases present and variance (P and F'). What phases will be present in each area of the diagram? What is the azeotrope composition of this mixture? At what temperatures the mixtures of the following compositions will boil (here, x_A is the mole fraction of acetone in the liquid mixture): (i) pure chloroform; (ii) $x_A = 0.15$; (iii) azeotrope; (iv) $x_A = 0.80$; (v) pure chloroform? What will be the compositions of the vapor phase produced when boiling takes place in each case?



5. Derive expressions for $\left(\frac{\partial S}{\partial V}\right)_T$ for the perfect gas and van der Waals gas

 $(p = \frac{RT}{V_m - b} - \frac{a}{V_m^2})$. For an isothermal expansion, for which kind of gas will ΔS be greater? Explain your conclusion.

Exam II CHM 3410, Dr. Mebel, Fall 2017 (Each problem is 20 pts.)

1. The vapor pressure of liquid ethanol is 7615 Pa at 298.15 K and $\Delta_{vap}H = 38.56$ kJ mol⁻¹. Calculate the normal and standard boiling points of ethanol.

2. At 39°C, a solution of ethanol ($x_A = 0.9006$, $p_A^* = 130.4$ Torr) and isooctane ($p_B^* = 43.9$ Torr) forms a vapor phase with the mole fraction of ethanol $y_A = 0.6667$ at a total pressure of 185.9 Torr.

- (a) Calculate the activity and activity coefficient for each component.
- (b) Calculate the total vapor pressure that the solution would have if it were ideal.
- (c) Is mixing of liquid ethanol and isooctane exothermic or endothermic? Justify your answer both qualitatively and quantitatively (based on Margules equations assuming that the solution is approximately regular). Is the assumption that the solution is regular accurate in this case?

3. 4.55 g of glucose ($C_6H_{12}O_6$) are dissolved in 1 kg of H₂O at 298.15 K. The density of water at this temperature is 997 kg m⁻³. The solution is placed in an osmotic pressure apparatus with semi-permeable membrane that permits the flow of H₂O, but not the solute, between compartments. Compute the osmotic pressure of this solution. How high will be the liquid in the column when the equilibrium is established?

4. Please, see below the liquid-vapor phase diagram of the ethanol/water mixture at p = 1 atm. Mark each area of the phase diagram with the number of phases present and variance (P and F'). What phases will be present in each area of the diagram? What is the azeotrope composition of this mixture? At what temperatures the mixtures of the following compositions will boil (here, x_A is the mole fraction of ethanol in the liquid mixture): (i) pure water; (ii) $x_A = 0.21$; (iii) $x_A = 0.62$; (iv) azeotrope; (v) pure ethanol? What will be the compositions of the vapor phase produced when boiling takes place in each case?



virial equation of state,
$$p = \frac{nRT}{V} \left(1 + \frac{nB}{V}\right)$$
, assuming here for simplicity that the

virial coefficient *B* is independent of temperature. For an isothermal expansion, for which kind of gas will the change in entropy ΔS be greater? Explain your conclusion. How your answer depends on the sign of the virial coefficient *B*?

Exam II CHM 3410, Dr. Mebel, Fall 2013 (Each problem is 20 pts.)

1. Carbon tetrachloride melts at 250 K. The vapor pressure of the liquid is 10539 Pa at 290 K and 74518 Pa at 340 K. The vapor pressure of the solid is 270 Pa at 232 K and 1092 Pa at 250 K.

- (a) Calculate $\Delta H_{\text{vaporization}}$ and $\Delta H_{\text{sublimation}}$.
- (b) Calculate ΔH_{fusion} .

(c) Calculate the normal boiling point and $\Delta S_{\text{vaporization}}$ at the boiling point.

Clausius - Clapeyron (a) equation applies both solid-gas phase boundaries. liquid-gas and Juap F Ch vap 8 31447 290K 07 kJ mol Asub H KJmol 270 37.44 8 314 232 250 k 5.37 Avap H A fus H = Asub H-Normal occu point 1 atm = 101325Pa vapor ussure P3= ln 13 3 Vap 8.3144 1 340 1 Svap = Duapt

2. The average human with a body weight of 70 kg has a blood volume of 5.00 L. The Henry's law constant for the solubility of N_2 in water is 9.04×10^4 bar at 298 K. Assume that this is also the value of the Henry's law constant for blood and that the density of blood is 1.00 kg L⁻¹.

- (a) Calculate the number of moles of N₂ absorbed in this amount of blood in air of composition of 80% N₂ at sea level, where the pressure is 1 bar, and at a pressure of 50 bar.
- (b) Assume that a diver was breathing compressed air at a pressure of 50 bar and then was suddenly brought to the sea level. What volume of N₂ gas was released as bubbles in the diver's bloodstream?

(a) p=1 bar pr= 0.8.p= 0.8 bar $PN_2 = \mathcal{X}_{N_2} \cdot K \qquad \mathcal{X}_{N_2} = \frac{PN_2}{K} = \frac{0.8}{904}$ Henry's law: XN2 = 8.85×10-6 Assuming that Blood has the same density and molar mass as water, we have 5 kg of <u>5 Kg</u> = 277.47mol 18.02×10⁻³ Kg·mol⁻¹ Solvent. MH20 = NN2 = XN2 NH20 = 2.455×10 md 50 At 50 bar, PNe, 2CN2 Cause ANNO and hence NN2 are a NH20+ NN2 ~ NH20) Factor of 50 higher: NNº (50 bar) = 0.123 mol (6) When pressure suddenly decreases back to I bar, the excess N2 is released to the gas phase: NN2 (gas) = NN2 (50 bar) - NN2 (1bar) = 0.1203 mg $V = N_{N_2}(gas) RT = 2 98 \times 10^{-3}$ PV = NN2(gas) RT

3. A sample of glucose (C₆H₁₂O₆) of mass 4.55 g is placed in a test tube of radius r = 2.50 cm. The bottom of the test tube is a membrane that is semipermeable to water. The tube is partially immersed in a beaker of water at 298 K so that the bottom is only slightly below the level of the water in the beaker. The density of water at this temperature is 997 kg m⁻³. After equilibrium is reached, how high is the water level of the water in the tube above that in the beaker. What is the value of the osmotic pressure? Assume that the test tube is cylindrical and the volume of the solution in the tube can be calculated as $V = \pi r^2 h$ and that the density of the solution in the tube is equal (approximately) to the density of water.

Osmotic prassure: IV = NRRT II = Sgh - hydrostatic pressure V= TINch PghJIPRh = MBRT h 2gTh = NBRI h = 1 RBRT $h_{B} = \frac{m_{gluc}}{M_{gluc}} = \frac{4.55}{180} \frac{g_{mol}}{g_{mol}} = 0.025 \text{ mol}}{h = \frac{1}{2.50 \times 10^{-2} m}} = \frac{1.80}{997.9.81.3.14} = \frac{1.806}{1.806} m$ $\Pi = Sgh = 997 kgm^{-3} \cdot 9.81 m \cdot 5^{-2} \cdot 1.806 m$ = 17663.9 Pa = 17.66 k Pa

4. The phase diagram for two metals A and B contains one eutectic and no compound between A and B forms. The freezing points of solutions of A and B are found to vary linearly with the mole fraction of B in the solution. The melting points of pure A and B are 650 K and 600 K, respectively. The cooling curve for a mixture containing 40% mole fraction of B exhibits a single flat region (eutectic halt) at 400 K. Using this information, sketch the A-B phase diagram and indicate the phases present in each region.

liquid molten P=1650 K 600 K 0=2 tiquia + solid 400K P=2 A + solid 50 lio 0.4 D

5. Describe how Le Chatelier's principle is manifested in changes of equilibrium constant (or equilibrium composition of a reaction mixture) with temperature and pressure. Support your explanation with formal equations showing the described changes.

Main points that should have been reflected in your answer 1) Formulate Le Chatelier's principle 2) Describe how K changes with temperature for exothermic and endothermic reactions (according to van't MoSS equation) and demonstrate that the changes occur in accordance with Le Chatelier's properiple. 3) Diszcuss that K is independunt of pressare but the composi-tion (partial pressures) at equilibrium may change. Take an example like A > 2B and consider how the composition changes with pressure and demonstrate that the changes occur in accordance with Le Chatelier's principle.

Clausius - Clapeyron equation: $ln \frac{Pa}{P1} = -\frac{\Delta vapH}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$ $\frac{1}{T_2} = -\frac{R}{\Delta vap}H lh \frac{P_2}{P_1} + \frac{1}{T_1}$ $T_{2} = \frac{1}{\frac{1}{T_{1}} - \frac{R}{\Delta_{vap}H} \ln \frac{P_{2}}{P_{1}}}$ $T_{1} = 373.12 \text{ K} \quad p_{1} = 760 \text{ Torr} \quad p_{2} = 461 \text{ Torr}$ <u>1</u> <u>1</u> <u>8.31447 J·K mol</u> <u>373.12 K</u> <u>40.656·10³ J moe⁻¹ ln <u>461 Tour</u> <u>760 Tour</u></u> T2 = $T_2 = 359.41 \text{ K}$

 $Q_{A} = \frac{P_{A}}{P_{A}^{*}} = \frac{J_{A}}{P_{A}} = \frac{0.6667 \cdot 189.9}{130.4}$ $J_{A} = \frac{Q_{A}}{Z_{A}} = \frac{0.95}{0.9006} = \frac{1.055}{1.055}$ -=0,95 a) $a_{B} = \frac{PB}{PB} = \frac{BP}{PB} = \frac{(1 - g_{A})P}{PB} = \frac{(1 - 0.6667) \cdot 185.9}{43.9}$ $a_{B} = 1.411$ $\chi_{B} = \frac{\alpha_{B}}{x_{B}} = \frac{\alpha_{B}}{1 - x_{A}} = \frac{1.411}{1 - 0.9006} = \frac{14.199}{1 - 0.9006}$ b) PA = 2CAPA = 0. 9006 · 130.4 = 117.4 Tom $PB = \mathcal{X}_{B} PB^{*} = (1 - \mathcal{X}_{A}) PB^{*} = (1 - 0.9006) \cdot 43.9$ PB = 4.4 Torr p = PA + PB = 121.8 Torr

I = [B] KT $[B] = \frac{h_B}{V} = \frac{3g/344.2 g \text{ mol}^{-1}}{1 \text{ kg} / 999.97 \text{ kgm}^3}$ $[B] = 8.7156 \mod m^{-3}$ II = 8.7156 mol. m⁻³. 8.31447 JK mol. 298.15K II = 21.605 k Pa = 162.05 Torz $\Pi = \rho g h$ 21.605.10³ Pa 999.97 kgm⁻³.9.81 m s⁻² $h = \frac{\Pi}{Sg} =$ h = 2.2 m

4. Please, see below the liquid-vapor phase diagram of the acetone/chloroform mixture at p = 1 atm. Mark each area of the phase diagram with the number of phases present and variance (P and F'). What phases will be present in each area of the diagram? What is the azeotrope composition of this mixture? At what temperatures the mixtures of the following compositions will boil (here, x_A is the mole fraction of acetone in the liquid mixture): (i) pure chloroform; (ii) $x_A = 0.15$; (iii) azeotrope; (iv) $x_A = 0.80$; (v) pure chloroform? What will be the compositions of the vapor phase produced when boiling takes place in each case?

F=C-P+Z

T-xy diagram for ACETONE / CHLOROFM (i) 61°C 3 (PRES = 1.013250 BAR) (ii) 63°C $T-\gamma$ (PRES = 1.013250 BAR) 23 (111) 64.2% 62 (iv) 59.5° Temperature C (v) 56.2°(6 8 0 Liquid /Vapor = 1 phase ß 57 0.7 0.8 0.9 D 0.1 0.3 0.4 0.5 0.6 0.2 MOLEFRAC ACETONE phase Azeotrope Composition: 10.35 Acetone Vapor 0.65 Chloroform Composition of Vapor phases @ boiling (i) O Acetone, I Chloreform U (ii) 0.10 Acetore, 0.90 chloroform (iii) 0.35 Acetore, 0.65 chloro form (iv) 0.875 Acetone, 0.125 Chloroform (v) 1 Acetore, O chloroform. 1/

Use the Maxwell relation: (5) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ $porfect gas: p = \frac{RI}{Vm}$ $\begin{pmatrix} \frac{\partial S}{\partial V} \\ \frac{\partial V}{T} \end{pmatrix} = \begin{pmatrix} \frac{\partial P}{\partial T} \\ \frac{\partial T}{V} \end{pmatrix} = \begin{pmatrix} \frac{R}{V_m} \end{pmatrix}$ $valt der Waals gas: p = \frac{RT}{V_m - 6} - \frac{\alpha}{V_m^2}$ $\begin{pmatrix} \frac{\partial S}{\partial V} \end{pmatrix}_{T} = \begin{pmatrix} \frac{\partial P}{\partial T} \end{pmatrix}_{V} = \begin{pmatrix} \frac{R}{V_{m} - 6} \end{pmatrix}$ For isothermal expansion $dS = \left(\frac{\partial S}{\partial V}\right)_T dV$ $dS = \frac{R}{V} dV - perfect gas$ $dS = \frac{R}{V_m - 6} dV - van der Waals gas$ Since 6 > 0 in vdW equation, R < R and hence the Vm < Vm-b AS will be greater for vd W gas.

Exam II CHM 3410, Dr. Mebel, Fall 2017 (Each problem is 20 pts.)

1. The vapor pressure of liquid ethanol is 7615 Pa at 298.15 K and $\Delta_{vap}H=38.56$ kJ mol⁻¹. Calculate the normal and standard boiling points of ethanol.

 $= -\frac{\Delta v_{ap}H}{P}$ R Ch P2/P1 A, mar H Avapt $= \frac{1}{T_1} - \frac{R \ln Pa/P_1}{\Delta vap H}$ 72 = 7615 Pa $T_1 = 298.15 K$ = 1 atm = 101 325Pal normal pressure) <u>1 8.31447 (h 7615</u> 298.15 38560 2 = To = 357,66 K - normal boiling point Pa = 1 bar = 100000 Pa (standard pressure) 1 298.15 - 8.31447 Ch (100000) 1 38560 TR= T2 = 357.30 K - standard boiling point

2. At 39°C, a solution of ethanol ($x_A = 0.9006$, $p_A^* = 130.4$ Torr) and isooctane ($p_B^* = 43.9$ Torr) forms a vapor phase with the mole fraction of ethanol $y_A = 0.6667$ at a total pressure of 185.9 Torr.

- (a) Calculate the activity and activity coefficient for each component.
- (b) Calculate the total vapor pressure that the solution would have if it were ideal.(c) Is mixing of liquid ethanol and isooctane exothermic or endothermic? Justify
- your answer both qualitatively and quantitatively (based on Margules equations assuming that the solution is approximately regular). Is the assumption that the solution is regular accurate in this case?

(a)
$$a_{A} = \frac{p_{A}}{p_{A}^{*}}$$
 $p_{A} = y_{A} \cdot p = 0.6667 \cdot 185.9 Tour = 123.9 Tour = 12.0 Tour$

6) Preal (185.9 Torn) > Pideal (101.57 Tour) There is a higher tendency for molecules to escape to the vapor phase than from ideal solution. Therefore, the solution is destable compared solution = mixing in Cin....... un favorale

Margules equations: 1) $ln f_A = \beta \alpha \beta$ 2) $ln f_B = \beta \alpha \beta$ 3) $ln f_B = \beta \alpha \beta$ 4) $\beta = \frac{ln f_A}{\alpha \beta} = 5.419$ $\beta = \frac{ln \delta \beta}{\alpha \beta} = 3.271$ $\alpha \beta^2 = 3.271$ For regular solution, both equations Should be valid and hence, the same value of B should be obtained from both of them More, we obtained rather different values of & from the two equations Therefore, the solution deviates From a regular solution. H = NBRT &A RB B>O => enthaloy of mixing HE>O Mixing is endothermic.

3. 4.55 g of glucose ($C_6H_{12}O_6$) are dissolved in 1 kg of H₂O at 298.15 K. The density of water at this temperature is 997 kg m⁻³. The solution is placed in an osmotic pressure apparatus with semi-permeable membrane that permits the flow of H₂O, but not the solute, between compartments. Compute the osmotic pressure of this solution. How high will be the liquid in the column when the equilibrium is established?

 $Oshaotic pressure: \Pi = RT [B]$ $[B] = \frac{Nglacose}{V_{H_2O}} = \frac{Mglucose}{M_{H_2O}} / \frac{Mglucose}{M_{H_2O}}$ $\begin{bmatrix} B \end{bmatrix} = \frac{4.55g / 180.156g \cdot moe^{-1}}{1 \, \text{kg} \, \text{/} \, 997 \, \text{kg} \, \text{m}^{-3}} = 25.18 \, \text{mol} \, \text{m}^{-3}$ [7 = 8.31447 J.K. mol - 298.15 K . 25.18 molim-3 $\int J = \frac{62420.5}{2} \, Pa = 0.640 \, atm = 468.2 \, Torr$ II = Pgh $h = \frac{51}{99} = \frac{62420.57a}{997 \text{ kg} \text{ m}^3 \cdot 9.81 \text{ m} \text{ s}^2} = \frac{6.382 \text{ m}}{997 \text{ kg} \text{ m}^3 \cdot 9.81 \text{ m} \text{ s}^2}$ Clearly, you need a very high column here for water not to spill over!

4. Please, see below the liquid-vapor phase diagram of the ethanol/water mixture at p = 1 atm. Mark each area of the phase diagram with the number of phases present and variance (P and F'). What phases will be present in each area of the diagram? What is the azeotrope composition of this mixture? At what temperatures the mixtures of the following compositions will boil (here, x_A is the mole fraction of ethanol in the liquid mixture): (i) pure water; (ii) $x_A = 0.21$; (iii) $x_A = 0.62$; (iv) azeotrope; (v) pure ethanol? What will be the compositions of the vapor phase produced when boiling takes place in each case?

Deta loken from Ozehmund Data Bark



5. Derive expressions for $\left(\frac{\partial S}{\partial V}\right)_T$ for the perfect gas and a real gas described by the

virial equation of state,
$$p = \frac{nRT}{V} \left(1 + \frac{nB}{V} \right)$$
, assuming here for simplicity that the

virial coefficient B is independent of temperature. For an isothermal expansion, for which kind of gas will the change in entropy ΔS be greater? Explain your conclusion.

How your answer depends on the sign of the virial coefficient B?

Using one of the Maxwell relations, we can write $(\frac{2S}{\partial V})_T = (\frac{2P}{\partial T})_V$ perfect gas: p = nRT, $(2P)_V = NR$ $\left(\frac{\partial S}{\partial V}\right)_T = \frac{n}{\sqrt{2}}$ Virial gas: $p = hkT + h^2 kTB$ $\left(\frac{\partial P}{\partial T}\right)_{V} = \frac{nk}{V} + \frac{h^2 kB}{V^2} = \left(\frac{\partial S}{\partial V}\right)_{V}^{2}$ $\left(\frac{\partial P}{\partial T}\right)_{V} = \frac{nk}{V} + \frac{h^2 kB}{V^2} = \left(\frac{\partial S}{\partial V}\right)_{V}^{2}$ Change of entropy in isothermal expansion: change of entropy in isothermal expansion: $dS = \left(\frac{\partial S}{\partial V}\right)_{T} dV$ $\Delta S = \int_{V_{i}}^{V} \left(\frac{\partial S}{\partial V}\right)_{T} dV$ $porfect gas: \Delta S = \int_{V_{i}}^{V} nkt dV = nk ln \frac{VF}{V_{i}}$ Virial gas: $\Delta S = \int_{V_i}^{V_f} \left(\frac{nR}{V_i} + \frac{n^2RB}{V_i}\right) dV =$ $= h R \ln \frac{V_f}{V_i} + h R^2 B \left(\frac{1}{V_i} - \frac{1}{V_f}\right)$ For expansion $(V_f > V_i): \Delta S_{virial} > \Delta S_{parfect, if}$ △ Svirial < △ Sperfect, if BLO 5