Science, Chemistry

Page 1 of 10 5. 111 Principles of Chemical Science EXAM # 3

=== Write legibly your name and your TA's name below. Do not open the exam until the start of the exam is announced. The exam is closed notes and closed book. You have 50 minutes (1 academic hour) to complete it. â—� Read each part of each problem carefully. â—� Write your answers legibly in the corresponding spaces of the attached sheets. â—� For problems requiring calculations, you must show these calculations clearly and indicate all values, including physical constants used to obtain your quantitative result. Significant figure and unit usage must be correct. â—� If you do not understand what the problem is asking, raise your hand and a proctor will come to your desk. â—� Some relevant equations and the periodic table are given on the last two pages. You may detach these pages once the exam has started.

=== 1. (22 points) _____ 2. (12 points) _____ 3. (27 points) ____ 4. (15 points) _____ 5. (24 points) _____ Total (100 points) _________________ Your Name(print): ___ANSWER KEY Your TA's Name (print): ___________________ Fall 2009, 5. 111 Exam #3 solution key Problem 1 (22 points total; 2 points each question). Page 2 of 10 Give one example of each of the following: (i) a pure liquid with an extremely low surface tension Answer: any molecule with low interatomic/intermolecular interactions Examples include — liquid He, Li, H2, (ii) a strong Lewis base Answer: Any Group I or Group II hydroxide e. g., LiOH, NaOH, KOH, Ca(OH)2 (iii) a pure substance which can be melted by reducing pressure at a given temperature Answer — Almost any compound but water; examples include sulfur, N_2, phosphorus, CO_2 (iv) an important colligative property of solutions Answer: vapor lowering pressure, boiling point elevation, freezing point depression, osmosis (v) a pure substance with no intermolecular (interatomic) London forces Answer: No such thing — all atoms and molecules have London forces (but H^+ and ideal gases are exceptions) (vi) a molecular solid with no intermolecular hydrogen bonding Answer: Any molecule that does not contain a H bonded to N, F, O and is a molecular solid Examples include: I_2, naphthalene, dry ice (CO_2), wax (vii) a pure substance whose solubility in water drops as the temperature is raised Answer: Almost any gas, e. g., O_2, H_2, N_2, Cl_2, Ne, Ar (viii) a good solvent for ethanolamine, $H_2NCH_2CH_2OH$ Answer: Almost any polar, hydrogen-bonding solvent; examples include water, ethanol, methanol (ix) a weak polyprotic acid Answer: examples include H_3PO_4, H_2S, H_2SO_3, H_2CO_3 (x) a group of chemical compounds that increase the solubility of hydrophobic substances in water Answer: detergents (soaps) organic solvents (xi) a compound besides water capable of intermolecular hydrogen bonding Answer: Any compound that contains a H bonded to N, F or O. examples include: NH_3, ethanol, , glycerol, HF Fall 2009, 5. 111 Exam #3 solution key Problem 2 (12 points). Page 3 of 10 A buffer solution can be prepared by starting with a weak acid and converting some of it to its salt by titrating with a strong base. The fraction of the original acid that is converted to the salt is designated f. (a) (6 points) Derive an equation similar to the Henderson-Hesselbalch equation but expressed in terms of f rather than concentrations. Answer: Think of what happens in the reaction table: Assume you start with [HA]

Reaction HA(aq) + OH-1 (aq) A-1 (aq) + â†’ Initial [HA]0 f After Rx't [HA] 0 -f f H_2O (ï�¬) Henderson-Hesselbalch equation is pH = pKa + log ([base]/[acid]). In this particular instance, the base forms from the reaction of a weak acid with a strong base. Dividing both the numerator and the denominator under the logarithm by the initial concentration of the weak acid [acid]o, one obtains pH = pKa + log (f / 1 - f). (b) (6 points) What is the pH at the point in the titration of phenol, C_6H_5OH, where f = 0. 27 (pKa of phenol under the titration conditions is 10. 00)? Answer: âŽ›fâŽž pH = pK a + log âŽœ âŽ�1âˆ' f âŽŸ âŽ 0. 27 1 âˆ' 0. 27 = 10. 00 + log (0. 3699) = 10. 00 + log = 10. 00 âˆ' 0. 432 = 9. 57 Fall 2009, 5. 111 Exam #3 solution key Problem 3 (27 points). Page 4 of 10 Answer the following questions: (i) (3 points) Why is the triple point of water a better fixed point for establishing a thermometric scale than either the melting point of ice or the boiling point of water? Answer: Because the triple point of water, in contrast to its melting or boiling points, is exact and does not depend on pressure. (ii) (3 points) What is the molar concentration of pure ethyl alcohol, C_2H_5OH, at 20oC if its density at that temperature is 0. 789 g/mL? g , so in 100. 00 mL of solution, there is 100(0. 789 g) = 78. 9 g of ethanol mL Molar mass of ethanol = 2(C) +6(H)+1(O)= 46. 07 g mol-1 78. 9 g # of moles = = 1. 713 mol 46. 07 g mol-1 Answer: density = [ethanol] = # of moles 1. 713 mol = = 17. 1 M volume 0. 100 L (iii) (3 points) What is ethyl alcohol's (C_2H_5OH) molal concentration at 37oC? Answer: remember that molal concentration is mol kg-1 solvent Method one: Method two: ethanol molal conc= = 1. 713 mol âŽ› kg âŽž gâŽž âŽ› âŽœ 0. 789 âŽŸ (100. 0 mL) âŽœ 3 âŽŸ âŽ� âŽ� 10 g âŽ mL âŽ âŽ› 1 mol âŽž âŽ› 1000 g âŽž molal concentration = âŽœ âŽ� 46. 07

g âŽŸ âŽœ 1 kg âŽŸ âŽ âŽ� âŽ = 21. 71 mol kg âˆ’1 1. 713 mol 7. 89 x 10 - 2 kg = 21. 7 mol kg âˆ’1 (iv) (3 points) Why does vaporization occur only at the surface of a liquid until the boiling point temperature is reached? In other words, why doesn’t vapor form throughout the liquid at lower temperatures ? Answer: Because there is not enough energy (“ strength") to overcome the atmospheric pressure (to which the vapor pressure becomes equal only at the boiling point). vaporization occurs when there is an equilibrium between liquid and gas state. Vapor does not form throughout the liquid because the liquid pressure is too high or the gas pressure only at the surface is low. Fall 2009, 5. 111 Exam #3 solution key Page 5 of 10 (v) (4 points) What volume of 0. 606 M NaOH in water must be diluted with water to 1. 00 L to produce a solution with pH = 12. 85? Answer: NaOH is a strong base, therefore a source of OH-1: pH = 12. 85, then pOH = 14. 00 -12. 85 = 1. 15 [OH -1] = 10 âˆ’1. 15 = 7. 079 x 10 -2 M1V1 = M 2V2 (7. 079 x 10 M)(1. 00 L) = (0. 606 M) V -2 2 V2 = 0. 11622 L V2 = 0. 116 L (vi) (8 points) An equilibrium mixture at 1000 K contains 0. 276 mol of H2, 0. 276 mol of CO2, 0. 224 mol of CO, and 0. 224 mol of H2O. CO2(g) + H2(g) â†” CO(g) + H2O(g) a) (4 points) How does Kc for this reaction depend on the reaction volume? Explain briefly your answer. Answer: Kc for this reaction does not depend on the reaction volume V because Kc = [CO][H2O] / [CO2][H2]. Multiplying both the numerator and the denominator by V2, one arrives at Kc = 0. 224 mol x 0. 224 mol / 0. 276 mol x 0. 276 mol = 0. 659. b) (4 points) What are the values of Kc and Kp for this reaction at 1000 K? Answer: Kc is concentration equilibrium constant, Kp is the pressure equilibrium constant. For this particular reaction, Kc and Kp are the same. [CO][H 2O] = [0. 224][0. 224

] Kc = Kp = [CO2][H 2] [0. 276][0. 276] = 0. 65869 = 0. 659 (vii) (3 points) Why are titrations of weak bases with weak acids rarely, if ever, used in analyses? Answer: Because the stoichiometric points are not pronounced and are thus very difficult to determine. Consequently, Ka and Kb values are also very difficult to determine. Fall 2009, 5. 111 Exam #3 solution key Problem 4 (15 points). Page 6 of 10 An 0. 155-g sample of an Al-Mg alloy reacts with an excess of HCl(aq) to produce 0. 0163 g of H2. What is the mass percent of Mg in the alloy? (HINT: each metal in the alloy reacts with the acid to form the corresponding metal chloride and molecular hydrogen.) Answer: First write a reaction as written in the problem: Reaction Al-Mg (s) + Excess HCl (aq) â†’ H2 (g) + AlCl3 (aq) Initial 0. 155 g 0. 0163 g conditions We need to think of the production of the metal chlorides in parallel reactions: Reaction Al + 3 HCl (aq) â†’ 1. 5 H2 (g) + AlCl3 (aq) Mg + 2 HCl (aq) â†’ H2 (g) + MgCl2 (aq) + MgCl2 (aq) Now the point of adding excess HCl, is to ensure that the limiting reagent is the Al-Mg alloy. If the mass of Mg in the alloy is x g, then its number of moles is x/24. 3 moles. Therefore, the number of moles of Al in the alloy is (0. 155 — x)/27. 0 moles. Due to the stoichiometries of the reactions above the number of moles of H2 formed from the Mg in the alloy is x/24. 3 moles, and the number of moles of H2 formed from the Al in the alloy is 1. 5(0. 155 — x)/27. 0 moles. Since 0. 0163 g of H2 is produced, the number of moles of H2 is 0. 0163/2. 02 = 0. 00807, we can write the equation for the moles of H2 as follows: x/24. 3 + 1. 5(0. 155 — x)/27. 0 = 0. 00807 Solving this algebraic equation gives x = 0. 039 g. Therefore, the mass percent of Mg in the alloy is 100% x 0. 039 / 0. 155 = 25. 1%. Fall 2009, 5. 111 Exam #3 solution key Problem 5 (24 points total; 3

points each). Page 7 of 10 Characterize the following unrelated statements as true or false. If false, briefly explain why. (i) The liquid-vapor phase boundary comes to an abrupt end at the critical point. Answer: True (ii) For a pure substance, a heating curve must coincide with its cooling curve. Answer: False — think about supercooling — that is when the solution is cooled much quicker than normal, this makes the cooling curve different than the heating curve. (iii) With everything else being equal, chemical reactions with more negative Gibbs free energy values typically are faster than those with less negative values. Answer: False —Gibbs free energy is a thermodynamic process, has nothing to do with rates (this is kinetics) (iv) CH4 should exhibit greater deviations from the ideal gas behavior than SiH4. Answer: False — Since SiH4 is a larger molecule than CH4, it should have larger London Dispersion forces and therefore greater deviations from ideal gas behavior. Fall 2009, 5. 111 Exam #3 solution key Page 8 of 10 (v) When an alkaline aqueous solution is diluted to one-half of its original concentration at 25oC, the pH always decreases by 0. 30 units. False because for alkaline solutions between pH 7 and 8 the dissociation of water will bake an appreciable contribution. False — 14. 00 = pOH + pH, so at 25 0C, Kw = [OH-1][H3O+], if the solution is diluted by one-half, the two concentrations multiplied together must be equal. At basic concentrations, the [OH-1] > [H3O+] and if the solution is diluted by half, and approaches 10-7 M, then the solution will be neutral and no matter how much you dilute it, it will remain neutral. (vi) Adding any of the following salts will not appreciably affect the aqueous solubility of BaSO4 (which is very poorly soluble in water): LiBr, Na2S, BaCl2, K2SO3, Ca(NO3)2, Li2SO4, and

CH_3COOK. False — common ion effect, addition of Li_2SO_4 and $BaCl_2$ will reduce the aqueous solubility of $BaSO_4$ (vii) Depending on the strength of intermolecular interactions, the molar enthalpy of freezing of a pure liquid can be either positive or negative. False, it is always negative because heat is released when a liquid freezes. Recall that freezing is the opposite of melting whose molar enthalpy is always positive since it takes energy to overcome intermolecular interactions. (freezing is always going to give off energy (to go from liquid to solid, molecules are losing kinetic energy)) (viii) A concentrated aqueous solution of a salt formed by a strong acid and a strong base, as well as by a weak acid and a weak base, should be pH neutral at 25oC. False because the pH of a concentrated aqueous solution of a salt formed by a weak acid and a weak base can be both acidic and basic depending on the relative strengths of the corresponding acid and base. False: the equivalence point of a weak acid and weak base is not pH neutral at 25 0C. Fall 2009, 5. 111 Exam #3 solution key PV = n·R·T Page 9 of 10 (P + an2/V2)·(V — nb) = n·R·T Î” Hvaporization = Hm (vapor) - Hm (liquid) Î” Hfusion = Hm (liquid) - Hm (solid) Î” Hfusion = - Î” Hfreezing s = kHP Î” Hsublimation = Hm (vapor) - Hm (solid) Î” Hsolution = Î” HL + Î” Hhydration Î” G = Î” H - T·Î” S Psolvent = xsolvent· Posolvent Tb - Tbo = kb · molality Tfo - Tf = kf·molality Tfo - Tf = i · kf · molality Ï€ = i·R·T·c pH + pOH = pKw pKa + pKb = pKw pH = pKa + log([base]o/[acid]o) Î” G = -R·T ·lnK Fall 2009, 5. 111 Exam #3 solution key Page 10 of 10