

CHEM 36

General Chemistry

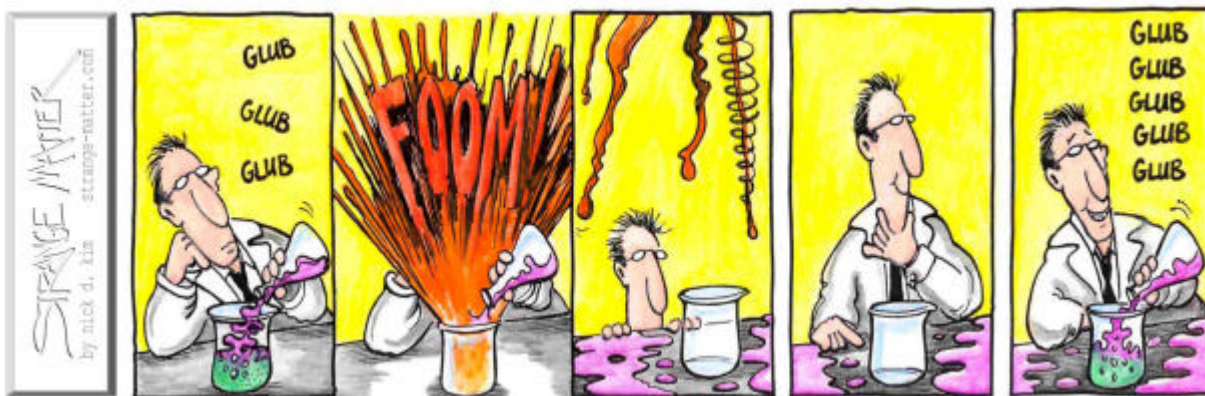
EXAM #1

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INSTRUCTIONS: Read through the entire exam before you begin. Answer all of the questions. For questions involving calculations, show **all** of your work -- **HOW** you arrived at a particular answer is **MORE** important than the answer itself! Circle your final answer to numerical questions.

The entire exam is worth a total of 150 points. Attached are a periodic table and a formula sheet jam-packed with useful stuff. Good Luck!



Page	Possible Points	Points Earned
2	20	20
3	15	15
4	20	20
5	25	25
6	15	15
7	30	30
8	25	25
TOTAL:	150	150

1. **[10 pts]** The sap in a maple tree can be described approximately as a 3.0% (by mass) solution of sucrose ($C_{12}H_{22}O_{11}$ - MW = 342.2948 g/mol) in water. If the density of the sap is 1.010 g/mL, and assuming that sap consists only of sucrose and water, calculate the molarity of sucrose in the sap.

We are given that the sap has a sucrose concentration of 3.0 %, which means that we know that there are 3.0 grams sucrose/100.0 grams sap

We want to get the *molarity*, so we need to convert the above concentration to moles sucrose/Liter sap

$$\frac{3.0 \text{ g sucrose}}{100.0 \text{ g sap}} \times \frac{1.010 \text{ g sap}}{\text{mL sap}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol sucrose}}{342.2948 \text{ g sucrose}} = 0.08852 \text{ mol/L}$$

Rounding to 2 sig figs, gives: 0.089 mol sucrose/L sap

2. **[10 pts]** The rising of sap in trees is caused largely by osmosis; the concentration of dissolved sucrose in sap is higher than that of the groundwater outside the tree. Calculate the osmotic pressure of a sap solution at 25.0 °C.

Using the molarity from the previous problem, we can use the osmotic pressure formula:

$$P = MRT$$

Substituting:

$$\begin{aligned} P &= (0.08852 \text{ mol/L})(0.08206 \text{ L-atm/mol-K})(298.15 \text{ K}) \\ &= 2.1658 \text{ atm} \\ &= \span style="border: 1px solid black; padding: 2px;">2.2 atm \end{aligned}$$

3. **[15 pts]** Maple syrup is the concentrated sap solution that results when most of the water is boiled off. If 40.0 liters of sap is boiled down to a volume of 1.00 liters (of syrup), what is the normal boiling point of the resultant syrup solution? (You may assume that the boiling process removes only water and that the sucrose does not react chemically during the boiling process. Recall, also, from problem #1 that sap is 97% water!)

The boiling point of pure water (the solvent in the sap and syrup) is 100.0 °C so we need to know how much the presence of the sucrose elevates the BP. So, we use the BP elevation equation which requires values for the BP elevation constant (K_b) and the molality of the sucrose in the syrup. The former is given to us and the latter must be calculated from the number of moles of sucrose and the mass (kg) of water remaining in the syrup.

First, the number of moles of sucrose is calculated from the sucrose *molarity* (in the sap) and the volume of sap used to make 1.00 Liter of syrup:

$$n_{\text{sucrose}} = 40.0 \text{ L} \times \frac{0.08852 \text{ mol sucrose}}{\text{L}} = 3.5408 \text{ mol sucrose}$$

Finding the mass of water remaining in the syrup is a 2-step process: first we determine the mass of water in 40.0 L of sap and then we subtract the amount of water that was boiled off to make the syrup (39.0 L = 39.0 kg).

If we know the volume of sap, then we can calculate the *mass* of the sap (using the density) and then, knowing that the sap is 97.0 % water, we can calculate the mass of water in the sap:

$$40.0 \text{ L sap} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{1.010 \text{ g sap}}{\text{mL}} \times \frac{97.0 \text{ g water}}{100.0 \text{ g sap}} = 3.9188 \times 10^4 \text{ g water}$$

So, the amount of water remaining in the syrup is:

$$3.9188 \times 10^4 \text{ g} - 3.90 \times 10^4 \text{ g} = 188.0 \text{ g water remaining in the syrup}$$

The molality of sucrose in the syrup is:

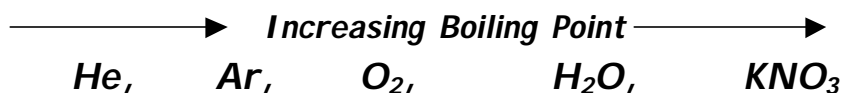
$$m = \frac{\text{mol sucrose}}{\text{kg water}} = \frac{3.5408 \text{ mol sucrose}}{0.1880 \text{ kg water}} = 18.834 \text{ mol sucrose/kg H}_2\text{O}$$

Finally:

$$\Delta T_b = K_b m = (0.512 \text{ K}\cdot\text{kg/mol})(18.834 \text{ mol/kg}) = 9.6430 \text{ K} (= 9.6430 \text{ }^\circ\text{C})$$

$$\text{So, } T_b = T_b^\circ + \Delta T_b = 100.0 + 9.6430 = 109.6430 \text{ }^\circ\text{C} \gg \boxed{110 \text{ }^\circ\text{C}}$$

4. [10 pts] Arrange the following substances in order of *increasing* normal boiling points and explain your reasoning: He, H₂O, Ar, KNO₃, O₂.



BP and magnitude of intermolecular forces are directly correlated:

He and Ar: Both noble gases, so very weak London Dispersion Forces hold them together (instantaneous dipole-induced dipole). Ar is more massive than He and more easily polarizable, so London Forces are larger.

O₂: Nonpolar, so London Forces dominate - larger than for He or Ar because molecule is bigger and, thus, more easily polarizable.

H₂O: Polar and can do Hydrogen bonding (10 - 100x stronger than London forces)

KNO₃: Ionic bond (ion-ion interaction) - about 10x stronger than H-bonding

5. [10 pts] The Henry's law constant at 25 °C for oxygen dissolved in water is 7.68 x 10² atm-L/mol. If the partial pressure of O₂ in the atmosphere is 0.20 atm, calculate the number of moles of O₂ dissolved in a liter of water.

According to Henry's Law:

$$P_{O_2} = K_{O_2}[O_2 (aq)]$$

Solve for concentration of O₂ (aq):

$$[O_2 (aq)] = P_{O_2}/K_{O_2} = 0.20 \text{ atm}/7.68 \times 10^2 \text{ atm-L/mol} = 2.6042 \times 10^{-4} \text{ mol/L}$$

So, in 1 L: 1 L x 2.6042 x 10⁻⁴ mol/L = 2.6 x 10⁻⁴ mol O₂

6. **[15 pts]** At 20 °C, the vapor pressure of toluene is 0.0289 atm and the vapor pressure of benzene is 0.0987 atm. Equal chemical amounts (equal number of moles) of toluene and benzene are mixed and form an ideal solution. Calculate the mole fraction of benzene and toluene *in the vapor* in equilibrium with this solution.

We are given the following data:

$$P_{\text{Toluene}}^{\circ} = 0.0289 \text{ atm} \quad C_{\text{Toluene}} = 0.500$$

$$P_{\text{Benzene}}^{\circ} = 0.0987 \text{ atm} \quad C_{\text{Benzene}} = 0.500$$

Using Raoult's Law, we can get the VP of each compound above the solution:

$$P_{\text{Toluene}} = C_{\text{Toluene}} P_{\text{Toluene}}^{\circ} = (0.500)(0.0289 \text{ atm}) = 0.01445 \text{ atm}$$

$$P_{\text{Benzene}} = C_{\text{Benzene}} P_{\text{Benzene}}^{\circ} = (0.500)(0.0987 \text{ atm}) = 0.04935 \text{ atm}$$

So, *in the vapor*, we can calculate the mole fraction for each compound by calculating the *vapor pressure fraction*:

$$C_{\text{Benzene}} = P_{\text{Benzene}} / (P_{\text{Toluene}} + P_{\text{Benzene}}) = 0.04935 \text{ atm} / (0.01445 \text{ atm} + 0.04935 \text{ atm})$$

$$C_{\text{Benzene}} = 0.04935 / 0.06380 = 0.77351 = \boxed{0.774} = C_{\text{Benzene}}$$

$$C_{\text{Toluene}} = 1 - C_{\text{Benzene}} = 1 - 0.77351 = 0.226489 = \boxed{0.226} = C_{\text{Toluene}}$$

7. **[10 pts]** Benzene and toluene are both mainly non-polar compounds. If instead of toluene, an equivalent chemical amount of a polar compound like benzoic acid were dissolved in benzene, how would you expect the partial pressure of benzene above the solution to deviate from the partial pressure of benzene above an ideal solution (if at all)? Explain.

Raoult's Law holds for an Ideal Solution: $P_{\text{Benzene}} = C_{\text{Benzene}} P_{\text{Benzene}}^{\circ}$

Adding a *polar* compound to a *non-polar* solvent will result in an *increased* intermolecular attraction between the (polar) solute and the (non-polar) solvent relative to the intermolecular attraction between a *non-polar* solute and the non-polar solvent. This will *reduce* P_{Benzene} , giving a negative deviation to Raoult's Law.

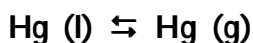
8. **[15 pts]** Mercury is the only metallic element that is a liquid at room temperature. Calculate the boiling point of mercury (°C). Some thermodynamic data that you might find helpful:

$$\Delta H_f^\circ [\text{Hg}(g)] = 61.40 \text{ kJ/mol}$$

$$S^\circ [\text{Hg}(l)] = 75.9 \text{ J/mol-K}$$

$$S^\circ [\text{Hg}(g)] = 175.0 \text{ J/mol-K}$$

First, let's write the equation for the vaporization of mercury:



We need values for $\Delta H_{\text{vap}}^\circ$ and $\Delta S_{\text{vap}}^\circ$:

$$\Delta H_{\text{vap}}^\circ = \Delta H_f^\circ [\text{Hg (g)}] - \Delta H_f^\circ [\text{Hg (l)}] = 61.40 \text{ kJ/mol} - 0 = 61.40 \text{ kJ}$$

$$\Delta S_{\text{vap}}^\circ = S^\circ [\text{Hg (g)}] - S^\circ [\text{Hg (l)}] = 175.0 \text{ J/mol-K} - 75.9 \text{ J/mol-K} = 99.1 \text{ J/K}$$

Ok, invoking Gibbs-Helmholtz:

$$\Delta G^\circ = \Delta H_{\text{vap}}^\circ - T_b \Delta S_{\text{vap}}^\circ$$

For a system in equilibrium: $\Delta G^\circ = 0$

$$0 = \Delta H_{\text{vap}}^\circ - T_b \Delta S_{\text{vap}}^\circ$$

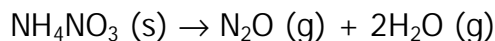
Solving for T_b :

$$T_b = \Delta H_{\text{vap}}^\circ / \Delta S_{\text{vap}}^\circ = 61.40 \times 10^3 \text{ J} / 99.1 \text{ J/K} = 619.5762 \text{ K}$$

Converting to Celsius:

$$T_b = 619.5762 \text{ K} - 273.15 \text{ K} = 346.4262 \text{ }^\circ\text{C} = \boxed{346. \text{ }^\circ\text{C}}$$

Ammonium nitrate can decompose to form dinitrogen oxide:



Some thermodynamic data that you might find helpful:

Compound	DH°_f (kJ/mol)	DG°_f (kJ/mol)
NH_4NO_3 (s)	-365.6	-183.9
N_2O (g)	82.1	104.2
H_2O (g)	-241.8	-228.6

a. [10 pts] Using the thermodynamic data provided, calculate the standard molar enthalpy change (ΔH°) for this reaction.

$$\begin{aligned}\text{DH}^\circ &= [\text{DH}^\circ_f (\text{N}_2\text{O}) + 2\text{DH}^\circ_f (\text{H}_2\text{O})] - \text{DH}^\circ_f (\text{NH}_4\text{NO}_3) \\ &= [82.1 \text{ kJ/mol} + 2(-241.8 \text{ kJ/mol})] - (-365.6 \text{ kJ/mol}) \\ &= -401.50 \text{ kJ} + 365.6 \text{ kJ} \\ &= \boxed{-35.9 \text{ kJ}}\end{aligned}$$

b. [5 pts] Based on the $\Delta\text{H}^\circ_{\text{rxn}}$ that you calculated above, is this process exothermic or endothermic?

exothermic endothermic (Circle One)

c. [10 pts] Calculate the change in standard molar free energy (ΔG°) at 25 °C for this process.

$$\begin{aligned}\text{DG}^\circ &= [\text{DG}^\circ_f (\text{N}_2\text{O}) + 2\text{DG}^\circ_f (\text{H}_2\text{O})] - \text{DG}^\circ_f (\text{NH}_4\text{NO}_3) \\ &= [104.2 \text{ kJ/mol} + 2(-228.6 \text{ kJ/mol})] - (-183.9 \text{ kJ/mol}) \\ &= -353.00 \text{ kJ} + 183.9 \text{ kJ} \\ &= \boxed{-169.1 \text{ kJ}}\end{aligned}$$

d. [5 pts] Based on the $\Delta\text{G}^\circ_{\text{rxn}}$ calculated in *part c*, is this reaction spontaneous process at 25 °C?

spontaneous not spontaneous (Circle One)

e. [5 pts] Would you expect ΔS° for this reaction to be positive or negative? (Don't do any calculations! Base your answer only on inspection of the reaction equation.) Briefly explain.

positive

negative

(Circle One)

Reactants are solid and the products are both gases, so the volume occupied by the compounds increases tremendously when going from reactants to products - greater volume means more microstates which translates to greater entropy.

f. [10 pts] Now, using the thermodynamic data provided, calculate the standard molar entropy change (ΔS°) for this reaction.

Invoking Gibbs-Helmholtz:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Solving for ΔS° :

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-35.9 \times 10^3 \text{ J} - (-169.1 \times 10^3 \text{ J})}{298.15 \text{ K}} = 446.755 \text{ J/K}$$

Rounding:

$$\Delta S^\circ = \boxed{446.8 \text{ J/K}}$$

g. [10 pts] Over what range of temperature (if any) is this reaction spontaneous?

Well, recall that ΔH° is negative and ΔS° is positive; for an *exothermic process* that results in an *increase in entropy* of the system, ΔG is *always negative*:

$$\Delta G = \Delta H^\circ - T\Delta S^\circ$$

So, the reaction will be spontaneous at ALL temperatures!

Extra Credit! -- 5 pts

You take a bottle of a soft drink out of your refrigerator. The contents are liquid and stay liquid, even when you shake them. Thirsty, you remove the cap, and the liquid freezes solid! Offer a possible explanation for this observation.

Gosh, that refrigerator must be cold! If the soft drink is cooled to a temperature that is *below* the FP of pure water, then the dissolved CO₂ could lower the FP of the soft drink so that it was still a liquid if the temperature was above the FP of the solution. When the bottle is opened, however, the dissolved CO₂ bubbles out of solution, decreasing the concentration of dissolved gas, and *raising* the FP of the solution. If the FP is raised to a temperature that is *greater* than the temperature of the solution, then it will freeze.