

Name \_\_\_\_\_ KEY \_\_\_\_\_ Rec. TA/time \_\_\_\_\_

1. (2 pts) The solubility of a solid solute is 32.3 g solute/100 g H<sub>2</sub>O at 20 °C. What minimum mass (in grams) of solute would need to be added to 13.1 g H<sub>2</sub>O at 20 °C to make the solution saturated?

Use solubility as a conversion factor to figure out how much solute would need to be in 13.1 g H<sub>2</sub>O to make it saturated.

$$? \text{ g solute} = 13.1 \text{ g H}_2\text{O} \times \frac{32.3 \text{ g solute}}{100 \text{ g H}_2\text{O}} = 4.23 \text{ g solute}$$

Thus, 4.23 g solute would be the amount of solute which could dissolve in 13.1 g H<sub>2</sub>O to give a saturated soln.

(**Note:** the **denominator** is **mass of solvent only** - don't confuse this with percent conc.)

**Saturated** soln. (see below).

A **saturated** solution occurs when the solution is in equilibrium with undissolved solute. Additional solute will not dissolve when added to a saturated solution. The solution contains the maximum amount of solute which can be dissolved in the solvent (it won't "hold" anymore solute). **Solubility** is the conc. of solute in a **saturated** soln. (the **maximum amount** that will dissolve, in (g solute)/(100 g solvent)). Even if you filter off the solution and get rid of the excess solid you still have a saturated solution. If you were to add more solid solute to the solution the solid will not dissolve.

An **unsaturated** solution has less than the maximum amount of solute dissolved in the solution (less solute than that needed to form a saturated solution). When you add more solute it will dissolve (i.e. an unsaturated solution can dissolve more solute).

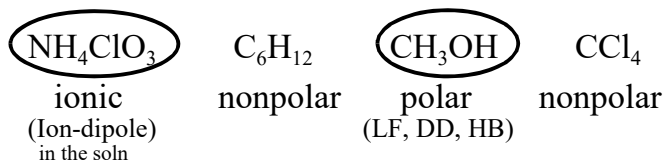
Since the conc. of solute (amount of solute) in this solution is 39 g/100 g H<sub>2</sub>O which is greater than the solubility of 32.3 g/100 g H<sub>2</sub>O (a saturated solution) the solution is **saturated** (greater than the maximum amount which can dissolve so there's 6.93 g solid on the bottom of the beaker).

A **supersaturated** solution actually has more solute dissolved than the saturated solution for a given temperature. How? Isn't the definition of a saturated solution such that it contains the maximum amount of dissolved solute for a given temp. and no more will dissolve? The answer to this question is yes, for a stable system. However, remember for most solids the conc. (solubility) increases as temperature increases. If you heat the system the solubility increases. Some substances have trouble crystallizing and if you are very careful and slowly cool the solution and don't disturb it you can get it to cool back to room temp. w/o the excess solid (which shouldn't be dissolved at room temp.) crystallizing out of solution. The excess solute and heat added can be "trapped" in the solution. This is a supersaturated solution and it is a **metastable** state. This means it's not the most stable state for the system. It will revert to the more stable state (saturated solution) over time or if disturbed by shaking, scratching the inner surface of the container or adding a "seed" crystal. This gives the excess solid a point of "nucleation" where the excess solute particles can attach and then start crystallizing out. As this happens the excess "trapped" heat is released to the surroundings. These types of solutions are often used in reusable hot packs. When the hot pack is kneaded in your hands the excess solute crystallizes releasing heat. When thrown in boiling water the supersaturated solution is reformed.

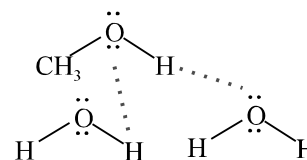
Also, don't confuse the terms concentrated and saturated or dilute and unsaturated. You can have a dilute saturated solution. If the solute is not very soluble then a saturated solution would be dilute. You can have a concentrated unsaturated solution. If the solute is very soluble you can have an unsaturated solution with a lot of solute dissolved which would then be concentrated.

Given a beaker with a liquid in it how could you tell if it's a saturated, unsaturated or supersaturated solution? Add some more solid. If none of it dissolves then the original solution was saturated. If some of it dissolves the original solution was unsaturated. If you add solid to the solution and more solid precipitates the original solution was supersaturated.

2. (4 pts) Which of the following are **soluble** in **water**,  $H_2O$ , and **WHY** (give a brief explanation dealing w. IAF & type of compound; ionic, polar, nonpolar for both solute and solvent)? (Circle all that apply.)



$H_2O$  is **polar** (LF, DD, H-bonding)



“Like Dissolves Like”

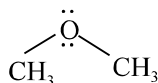
**nonpolar** solutes dissolve in **nonpolar** solvents  
**polar & ionic** solutes dissolve in **polar** solvents

The  $NH_4ClO_3$  is ionic and dissolves in polar  $H_2O$  as ions. So you get ion-dipole AF between the ions and the  $H_2O$  water molecules.

The  $CH_3OH$  is polar and forms LF, DD, HB as a pure substance.  $H_2O$  is polar and forms LF, DD, HB as a pure substance. So  $CH_3OH$  can form LF, DD, HB to the  $H_2O$  molecules.

3. (8 pts) When  $CH_3OCH_3$  dissolves in  $H_2O$  forces of attraction are being broken in the solute and in the solvent and attractive forces are formed between the solute and solvent. Answer the following questions concerning this process. (H, C, N and O are in groups 1A, 4A, 5A and 6A, respectively. H, C, N and O have 1, 6, 7 and 8 electrons, respectively.) **Explain your choices!**

- a) What forces of attraction are broken between  $CH_3OCH_3$  molecules? (solute-solute AF)

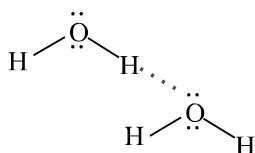


Bent around O (like  $H_2O$ ) => **polar**

LF (London Dispersion Forces)      DD (dipole-dipole AF)

(NO H-bonding in the pure substance between  $CH_3OCH_3$  molecules)

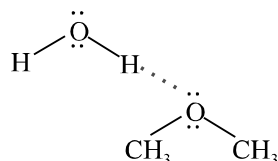
- b) What forces of attraction are broken between  $H_2O$  molecules? (solvent-solvent AF)



Bent => **polar** and **H on O** (w.  $lpe^-$  on O)

LF      DD      HB (H-bonding)

- c) What forces of attraction are formed between  $CH_3OCH_3$  and  $H_2O$  in forming the solution? (solute-solvent AF; “unlike” forces)



LF      form between both (only slightly weaker than LF that were broken)

DD      both are polar and can form DD AF to each other

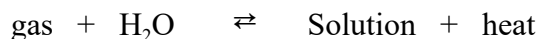
HB      from  $lpe^-$  on O in  $CH_3OCH_3$  to H in  $H_2O$

4. (2 pts) What happens to the solubility of a gas in water as temperature increases?

Not on Carmen quiz

Solubility of a gas in water decreases as temp. increases. We can explain the temp affect on a gas in water in two ways.

We can use Le Châtelier's Principle, as discussed in class. When a gas dissolves in water the  $\Delta H_{\text{soln}}$  is negative, heat is evolved.. When a change is made to a system at equilibrium the system shifts in a way to minimize the change. In a simple way for now (more in Ch 15) when you add something to a system at equilibrium it shifts to try to use up some of what's added. When you remove something from a system at equil. it shifts to try to replace some of what's removed.



So, this is at equil. at room temp and we bring a Bunsen burner up to heat and add heat (raise the temp.). Since heat is a product the system shifts away from what's added, in this case toward the reactants to use some of the heat that's being added. As it shifts left you get less solution (gas comes out of solution).

Another way to think about it is what happens to kinetic energy of the molecules when temp. changes. If you add heat to inc. the temp. the KE of everything increases. This is more important for the dissolved gas molecules. Since they have more KE they can escape more easily into the vapor phase above the solution and the gases solubility decreases.

5. (5 pts) You have a 0.0020 M aqueous  $\text{Fe}(\text{NO}_3)_3$  solution? Assuming an "ideal" ionic solution (i.e. no ion-pairing), what would be the **osmotic pressure** at  $30.0^\circ\text{C}$ ? **Show work or explain your answers.**

$$\Pi = i MRT = (M_{\text{particles}})RT \quad M_{\text{particles}} = i M_{\text{stated}}$$

for an "ideal" ionic solution,  $i = \#$  ions from formula for the compound  
(there is no ion-pairing between ions in the solution)



$$\Pi = 4 (0.0020 \text{ mol/L}) (0.08206 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(303.15 \text{ K}) = 0.1990 \text{ atm} = 0.20 \text{ atm (2 s.f.)}$$

(151 torr)

6. (4 pts) The freezing point of p-dichlorobenzene is 53.1 °C. A solution of 1.26 g of a sulfa drug in 10.0 g of p-dichlorobenzene freezes at 47.9 °C. What is the **molecular weight** of the sulfa drug? ( $K_f = 7.10^\circ\text{C}/m$ )

Whenever you want MW think of g/mol:  $MW = \frac{\text{mass}}{\text{moles}}$

have mass of 1.26 g, need moles (get from molality)

$$\Delta T_f = (i m_{\text{solute}}) K_f = m_{\text{particles}} K_f \quad m_{\text{particles}} = i m_{\text{solute}}$$

$i$  = # particles in solution (integer for ideal behavior)

= 1 for nonelectrolytes solutes (nondissociating or nonionizing)

= # particles resulting formula unit for ionizing/dissociating cmpds (ideal behavior)

$m_{\text{solute}}$  = stated molality of solute

$i * m$  = molality of particles

$K_f$  = freezing point depression constant (depends on solvent)

for an "ideal" ionic solution,  $i$  = # ions from formula for the compound  
(there is no ion-pairing between ions in the solution when it's behaving ideally)

For this form of the eqn;  $\Delta T_f = T_{f,\text{solvent}} - T_{f,\text{soln}}$  and is a positive value

The newer editions (13<sup>th</sup> and 14<sup>th</sup>) of the book use:

$$\Delta T_f = - (i m_{\text{solute}}) K_f = - m_{\text{particles}} K_f$$

where  $\Delta T_f = T_{f,\text{soln}} - T_{f,\text{solvent}}$  and is a negative number but it corresponds to final - initial as most delta values do.

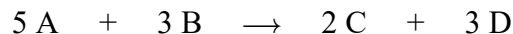
Normal f.p. of  $\text{C}_6\text{H}_4\text{Cl}_2 = 53.1^\circ\text{C}$     f.p. of soln = 47.9 °C     $K_f = 7.10^\circ\text{C}/m$

$$m = \frac{\Delta T_f}{K_f} = \frac{53.1^\circ\text{C} - 47.9^\circ\text{C}}{7.10^\circ\text{C}/m} = 0.7\mathbf{3}239 \text{ molal}$$

$$\text{mol solute} = 0.010\mathbf{0} \text{ kg } \text{C}_6\text{H}_4\text{Cl}_2 \times \frac{0.7\mathbf{3}239 \text{ mol}}{1 \text{ kg } \text{C}_6\text{H}_4\text{Cl}_2} = 0.007\mathbf{3}239 \text{ mol solute}$$

$$MW = \frac{1.26 \text{ g}}{0.007\mathbf{3}239 \text{ mol}} = 1\mathbf{7}2.03 \text{ g/mol} = 1\mathbf{7}2 \text{ g/mol} = 1.7 \times 10^2 \text{ g/mol (technically only 2 s.f.)}$$

7. (3 pts) For the reaction below, the rate of disappearance of reactant A ( $-\Delta[A]/\Delta t$ ) is 0.55 M/s. What is the rate of appearance of product C ( $\Delta[C]/\Delta t$ ) in M/s? **Show work or explain your answer.**



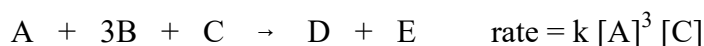
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$$\text{rate of rxn} = \frac{1}{5} \left( \frac{-\Delta[A]}{\Delta t} \right) = \frac{1}{3} \left( \frac{-\Delta[B]}{\Delta t} \right) = \frac{1}{2} \left( \frac{\Delta[C]}{\Delta t} \right) = \frac{1}{3} \left( \frac{\Delta[D]}{\Delta t} \right)$$

Relate THE rate of reaction to the rates in terms of disappearance of reactants or formation of products by using the reciprocal of the coefficients in the balanced eqn as multiples of the various rates.

$$\left( \frac{\Delta[C]}{\Delta t} \right) = \frac{2}{5} \left( \frac{-\Delta[A]}{\Delta t} \right) = \frac{2}{5} (0.55 \text{ M/s}) = 0.22 \text{ M/s}$$

8. (3 pts) For the reaction and rate law given below, which of the statements is **CORRECT**?



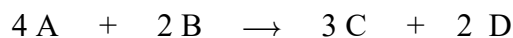
- 1) the reaction is fourth order overall
- 2) tripling [A] will increase the rate by a factor of 9
- 3) doubling [C] will increase the rate by a factor of 4
- 4) assuming the units for rate are M/s, the units for k would be  $M^{-3} \cdot s^{-1}$
- 5) tripling the rate constant, k, will increase the rate by a factor of 9

- a) 1, 2                      b) 1, 5                      c) 2, 3                      d)\* 1, 4                      e) 1, 4, 5

$$r = k [A]^3 [C]$$

- 1) **True:** overall order = 3 + 1 = 4 (add the order with respect to each compd that appears in rate law)
- 2) False: if [A] triples, rate inc by factor of  $3^3 = 27$
- 3) False: if [C] doubles, rate inc by factor of  $2^1 = 2$
- 4) **True:** Using units of M and s (seconds) solve for k and you get  $M^{-3} \cdot s^{-1}$
- 5) False: The rate and rate constant are directly proportional. When k triples the rate triples.

9. (12 pts) The following data were measure for the reaction



Experiment	[A] (M)	[C] (M)	Initial rate (M/s)
1	0.200	0.200	0.2000
2	0.600	0.200	5.4000
3	0.600	0.400	1.3500
4	0.200	0.400	0.0500
5	0.400	0.600	0.1778

- a) What is the **rate law** for the reaction?

$$r = k [A]^x [C]^y \quad \text{general rate law - find } x \text{ \& } y$$

$$\frac{r_j}{r_i} = \frac{k [A]_j^x [C]_j^y}{k [A]_i^x [C]_i^y} = \left( \frac{[A]_j}{[A]_i} \right)^x \left( \frac{[C]_j}{[C]_i} \right)^y \quad \text{will always look similar to this}$$

- 1) find order w/rsp to A (hold [C] constant) - use exp 1 & 2 (or 3 & 4 - [A] must chg)

$$\frac{r_2}{r_1} = \left( \frac{[A]_2}{[A]_1} \right)^x \left( \frac{[C]_2}{[C]_1} \right)^y \quad \frac{5.4000 \text{ M/s}}{0.2000 \text{ M/s}} = \left( \frac{0.600 \text{ M}}{0.200 \text{ M}} \right)^x \left( \frac{0.200 \text{ M}}{0.200 \text{ M}} \right)^y$$

$$27 = 3^x \Rightarrow x = 3 \quad \log 27 = \log 3^x \Rightarrow \log 27 = x \log 3 \Rightarrow x = (\log 27)/(\log 3) = 3$$

- 2) find order w/rsp to C (no need to hold [A] constant) - use exp 1 & 3 (any two - [C] must chg)

$$\frac{r_3}{r_1} = \left( \frac{[A]_3}{[A]_1} \right)^3 \left( \frac{[C]_3}{[C]_1} \right)^y \quad \frac{1.3500 \text{ M/s}}{0.2000 \text{ M/s}} = \left( \frac{0.600 \text{ M}}{0.200 \text{ M}} \right)^3 \left( \frac{0.400 \text{ M}}{0.200 \text{ M}} \right)^y$$

$$6.75 = (3)^3 (2)^y \Rightarrow 6.75 = (27) 2^y \Rightarrow 0.25 = 2^y \Rightarrow 1/4 = 2^y \Rightarrow y = -2$$

$$\log(0.25) = \log 2^y \Rightarrow \log(0.25) = y \log 2 \Rightarrow y = (\log 0.25)/(\log 2) = -2 \Rightarrow y = -2$$

- 3) Rate Law

$$r = k [A]^3 [C]^{-2}$$

**NOTE:** For step 2 above, when finding y (the order with respect to C) I did NOT have to hold [A] constant because I already knew it's power. I purposely used two exp. such that both substances changed conc. to show that once you know the exponent of a substance it no longer has to be held constant (last problem in the section of homework titled "Rate Laws", section 14.3). I did have to make sure I chose two exp. in which [C] changed.

**NOTE:** A product is in this rate law. That is fine. You can have reactants, products, catalysts and inhibitors in rates laws (we didn't see any examples of inhibitors in mechanisms but I have mentioned them - they slow down the reaction). Intermediates are different. When dealing with a mechanism you try to get rid of conc. of intermediates whenever possible.

\*\*\*\* Cont. on next page \*\*\*\*

9) (Cont.)

b) What is the reaction **order** with respect to each **compound** AND what is the **overall** reaction **order**?

order with respect to A = 3

order with respect to C = -2

overall order of the reaction = (3) + (-2) = **1** (first order overall)

c) What is the value of the **rate constant** (based on data from experiment 1)?

$$k = \frac{r_1}{[A]_1^3 [C]_1^{-2}} = \frac{0.2000 \text{ M/s}}{(0.200 \text{ M})^3 (0.200 \text{ M})^{-2}} = 1.00 \text{ s}^{-1}$$

10. (6 pts) The rate law for the decomposition of  $AB_2$  ( $AB_2 \rightarrow AB + \frac{1}{2} B_2$ ) is

$$r = (0.630 \text{ M}^{-1}\cdot\text{s}^{-1}) [AB_2]^2 \quad 2^{\text{nd}} \text{ order in } AB_2; \quad k = 0.630 \text{ M}^{-1}\cdot\text{s}^{-1}$$

a) (4 pts) If the initial concentration of  $AB_2$  is 3.00 M what will the **concentration** of  $AB_2$  be (in M) after 1.00 minute?

Want  $[AB_2]$  after 1.00 min (60.0 seconds) given  $[AB_2]_0 = 3.00 \text{ M}$

- use the **integrated rate equation** for a  $2^{\text{nd}}$  order reaction

Need to know the order of reaction; look at the rate law above - it is  $2^{\text{nd}}$  order in  $AB_2$

$$1/[A]_t = kt + 1/[A]_0$$

$$1/[AB_2]_t = kt + 1/[AB_2]_0$$

$$1/[AB_2]_{50.0 \text{ s}} = (0.630 \text{ M}^{-1}\text{s}^{-1}) (60.0 \text{ s}) + 1/3.00\text{M}$$

$$1/[AB_2]_{50.0 \text{ s}} = 38.13 = 38.1 \text{ M}^{-1}$$

$$[AB_2]_{50.0 \text{ s}} = 2.622 \times 10^{-2} \text{ M} = 2.62 \times 10^{-2} \text{ M} \text{ (3 s.f.)}$$

b) (2 pts) What is the rate after 1.00 minute?      Not asked for on the Carmen quiz.

Asked for the rate you need to use the rate law, not an integrated rate eqn. This problem asks for the rate after 1.00 minute. This means you need to use the integrated rate eqn. to get the conc. at 1.00 min and then use this conc. to get the rate.

After 1.00 min,  $[AB_2] = 2.622 \times 10^{-2} \text{ M}$

$$r = (0.630 \text{ M}^{-1}\cdot\text{s}^{-1}) [AB_2]^2 = (0.630 \text{ M}^{-1}\cdot\text{s}^{-1}) [2.62 \times 10^{-2} \text{ M}]^2$$

$$r = 4.332 \times 10^{-4} \text{ M}\cdot\text{s}^{-1} = 4.33 \times 10^{-4} \text{ M}\cdot\text{s}^{-1}$$

Compare this to the rate at the very start of the reaction when  $[AB_2] = 3.00 \text{ M}$ .

$$r = (0.630 \text{ M}^{-1}\cdot\text{s}^{-1}) [AB_2]^2 = (0.630 \text{ M}^{-1}\cdot\text{s}^{-1}) [3.00 \text{ M}]^2$$

$$r = 5.67 \text{ M}\cdot\text{s}^{-1}$$



11. (4 pts) The decomposition of AB ( $AB \rightarrow A + B$ ) is zero order in AB with a rate constant of  $1.10 \times 10^{-3} \text{ M}\cdot\text{s}^{-1}$ . If the initial concentration is 0.100 M at the very start of the reaction what is the second half-life (in minutes)?

half-life,  $t_{1/2}$ , is the time it takes for conc. to dec. to  $\frac{1}{2}$  of the previous conc.

For a zero-order reaction:  $t_{1/2} = [A]_0/(2k)$  (dependent on the initial conc)

$$t_{1/2} = 0.100\text{M}/\{2(1.10 \times 10^{-3} \text{ M}\cdot\text{s}^{-1})\} = 45.\underline{45} \text{ s} = 0.757\underline{5} \text{ min (takes 0.758 min for conc to dec. by } \frac{1}{2}\text{)}$$

This is the first half-life.

For zero-order reactions successive half-lives decrease (each is **half** of previous)

(takes less time for conc. to dec. by  $\frac{1}{2}$  each period)

So the 2<sup>nd</sup> half-life would be  $\frac{1}{2} (0.757\underline{5}/2 \text{ min}) = 0.378\underline{7} \text{ min} = \mathbf{0.379 \text{ min}}$

Half-lives (similar to #50 on Ch 14 extra practice problems handout)

$$1^{\text{st}} \text{ order: } t_{1/2} = 0.693/k \quad 2^{\text{nd}} \text{ order: } t_{1/2} = 1/(k [A]_0)$$

Both 0 (zero) and 2<sup>nd</sup> order half-lives depend on the initial conc of reactant, while 1<sup>st</sup> order does not.

\* Note\* The half-life for a 1<sup>st</sup> order rxn is independent of the conc. (i.e. the half-life for a particular rxn will be the same no matter what is the initial conc. and successive half-lives will be the same). This is not true for other orders, for which successive half-lives change.

$$\text{Zero-order} \\ \text{-----} \\ t_{1/2} = \frac{[A]_0}{2k}$$

DECREASES  
as rx. proceeds  
(successive  $\frac{1}{2}$ -lives  
get smaller -  $\frac{1}{2}$  previous  
e.g.  $t_{1/2,1} = 40 \text{ s}$   
 $t_{1/2,2} = 20 \text{ s}$   
 $t_{1/2,3} = 10 \text{ s}$ )

$$1^{\text{st}}\text{-order} \\ \text{-----} \\ t_{1/2} = \frac{0.693}{k}$$

CONSTANT  
as rx. proceeds  
(successive  $\frac{1}{2}$ -lives  
are same  
e.g.  $t_{1/2,1} = 40 \text{ s}$   
 $t_{1/2,2} = 40 \text{ s}$   
 $t_{1/2,3} = 40 \text{ s}$ )

$$2^{\text{nd}}\text{-order} \\ \text{-----} \\ t_{1/2} = \frac{1}{k[A]_0}$$

INCREASES  
as rx. proceeds  
(successive  $\frac{1}{2}$ -lives  
get larger - doubles  
e.g.  $t_{1/2,1} = 10 \text{ s}$   
 $t_{1/2,2} = 20 \text{ s}$   
 $t_{1/2,3} = 40 \text{ s}$ )