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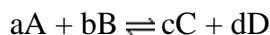
Lab Partners: \_\_\_\_\_

### DETERMINATION OF AN EQUILIBRIUM CONSTANT

By Thomas Cahill, Arizona State University, New College of Interdisciplinary Arts and Sciences.

Any chemical reaction will eventually proceed to a state of dynamic equilibrium, in which the reactants and products are present in definite concentrations. In some cases, the equilibrium will be attained only after nearly all of the reagents have been consumed and converted to reaction products. Such a reaction is said to "go to completion." Often a substantial fraction of the original reagent concentration remains after equilibrium has been achieved.

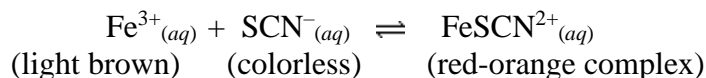
The system reaches an equilibrium state when the rate of the forward reaction is equal to the rate of the reverse reaction. The general equilibrium equation is as follows, where A,B,C,D are the involved chemical species and the lower case letters are the coefficients in the balanced chemical reaction:



And the equilibrium constant expression ( $K_{eq}$ ) is as follows:

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

This experiment will investigate the reaction of ferric ions with thiocyanate ions and the condition of equilibrium which results. The concentration of reactants and products remaining at equilibrium will be related to each other by a mathematical expression involving the equilibrium constant of the reaction. The two reactant ions, which are nearly colorless, react to form a red-orange colored complex - the ferric thiocyanate ion, as shown in the following equilibrium reaction:



The higher the concentration of the  $\text{FeSCN}^{2+}$ , the more intense is the red color of the solution. Thus, the color of the solution allows the experimenter to infer the amount of  $\text{FeSCN}^{2+}$  present, either by observing the solution visually, or more accurately, by using an absorption spectrophotometer. A spectrophotometer is an instrument that measures the fraction of an incident beam of light's intensity absorbed by a sample at a particular wavelength. For a given substance, the amount of light absorbed depends on the concentration, path length, wavelength of light, and the solvent. One method of expressing the amount of light absorbed is in terms of the **absorbance** ( $A$ ) of light by the sample. Beer's Law relates the amount of light being absorbed to the concentration of the substance absorbing the light by the following equation:

$$A = abC$$

where

- A= measured absorbance
- a = molar absorptivity constant
- b = path length through which the radiation passes
- C = molar concentration of the absorbing substance

Beer's law takes the form of a linear equation ( $y = mx + b$ ), so if the measured Absorbance ( $A$ ) is plotted on the Y axis and the molar concentration ( $C$ ) of the substance is plotted on the X-axis, a straight line will result with a slope ( $m$ ) equal to  $ab$ . Once the Beer's Law plot is created from a series of standard solutions, a new sample of unknown concentration can then be analyzed, and from its measured absorbance @ 445nm the concentration of the unknown can then be determined.

The reaction that we will be using is reversible and does not proceed to completion. How then can the concentrations of known  $\text{FeSCN}^{2+}$  solutions be determined? According to Le Chatelier's Principle, by preparing a solution in which the initial  $\text{Fe}^{3+}$  concentration is much larger than that of the  $\text{SCN}^-$ , we can drive the equilibrium far to the right so that virtually all of the  $\text{SCN}^-$  ions originally present will react to form the, red-orange,  $\text{FeSCN}^{2+}$  complex. Thus, the **moles of  $\text{SCN}^-$  consumed are equal to the moles of  $\text{FeSCN}^{2+}$  produced**. Dividing the moles of  $\text{FeSCN}^{2+}$  by the final volume of the solution in liters gives the concentration of the  $\text{FeSCN}^{2+}$ .

### Example 1:

When 1mL of 0.002M  $\text{SCN}^-$  is added to excess  $\text{Fe}^{3+}$  and diluted with water to a final volume of 25mL, the concentration of  $\text{FeSCN}^{2+}$  is:  $8.00 \times 10^{-5}$  M.

- **Initial moles  $\text{SCN}^-$ :**  $(0.00200 \text{ mol/L } \text{SCN}^-) \times (1 \text{ L}/1000 \text{ mL}) \times (1 \text{ mL}) = 2.00 \times 10^{-6} \text{ mol } \text{SCN}^-$
- **Molarity  $\text{FeSCN}^{2+}$ :**  $(2.00 \times 10^{-6} \text{ mol}) / (0.025 \text{ L}) = \mathbf{8.00 \times 10^{-5} \text{ M } [\text{FeSCN}]^{2+}}$

The measured absorbance of a  $\text{FeSCN}^{2+}$  equilibrium solution and the Beer's Law calibration curve allows the equilibrium concentration of  $\text{FeSCN}^{2+}$  to be calculated. With this information and the initial concentrations of  $\text{Fe}^{3+}$  and  $\text{SCN}^-$ , the final equilibrium concentrations of all species can be calculated. The value of the equilibrium constant ( $K_{eq}$ ) is then calculated as illustrated below in Example 2.

### Example 2:

The equilibrium concentration of  $\text{FeSCN}^{2+}$  was determined using a Beer's Law plot to be  $6.08 \times 10^{-5}$  M in a solution that initially was  $1.00 \times 10^{-3}$  M in  $\text{Fe}^{3+}$  and  $2.00 \times 10^{-4}$  M in  $\text{SCN}^-$ . Calculate the value of  $K_{eq}$ .



	$\text{Fe}^{3+}$	$\text{SCN}^-$	$\text{FeSCN}^{2+}$
Initial	$1.00 \times 10^{-3} \text{ M}$	$2.00 \times 10^{-4} \text{ M}$	0
Change	$-6.08 \times 10^{-5} \text{ M}$	$-6.08 \times 10^{-5} \text{ M}$	$+6.08 \times 10^{-5} \text{ M}$
Equilibrium	$9.39 \times 10^{-4} \text{ M}$	$1.39 \times 10^{-4} \text{ M}$	$6.08 \times 10^{-5} \text{ M}$

$$K_{eq} = \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]} = \frac{6.08 \times 10^{-5}}{(9.39 \times 10^{-4})(1.39 \times 10^{-4})} = 466$$

In Part A of this lab you will measure the absorbance of a series of solutions with known  $\text{FeSCN}^{2+}$  concentrations in order to prepare a calibration curve. In Part B, you will prepare some equilibrium solutions and determine the equilibrium constant for the reaction.

## EXPERIMENTAL PROCEDURE

### Part A – The Calibration Curve:

#### Skip the grayed procedure for the online labs

Go to <https://www.public.asu.edu/~jhwang43/>

Click on “General Chemistry II Laboratory Exercises, By Thomas Cahill”

Click on “Lab4: Determination of an Equilibrium Constant”

Click on “Part A: The Calibration Curve:”

- Prepare the 5 standard solutions as follows:

Standard Solution #	Volume 0.2M $\text{Fe}^{3+}$	Volume 0.002M $\text{SCN}^-$	Total volume (Dilute w/DI)
1	5.00mL	0.00mL	25mL
2	5.00mL	1.00mL	25mL
3	5.00mL	2.00mL	25mL
4	5.00mL	3.00mL	25mL
5	5.0 mL	4.00mL	25mL

1. Obtain about 35mL of the 0.2M  $\text{Fe}^{3+}$  solution and 25mL of 0.002M  $\text{SCN}^-$  in separate 100mL beakers from the reagent stations and bring them back to your station, **by clicking on “Click to Add ~35 mL 0.2 M  $\text{Fe}^{3+}$  Solution to the 100 mL Beaker Below”, and by clicking on “Click to Add ~25 mL 0.002 M  $\text{SCN}^-$  Solution to the 100 mL Beaker Below”**. Label the solutions! Place a clean pipette tip into each beaker (point down). You will be using one automatic pipette for the experiment and you will need to exchange the tips in order to measure each reagent.
2. For standard solution #1, check that the auto-pipette to 1 mL (1000  $\mu\text{L}$ ) and attach a tip. Measure 5mL of  $\text{Fe}^{3+}$  into a clean 25mL volumetric flask, **by clicking “Click to Add DI Water to Have a Total 25mL in the Volumetric Flask Below”**. Follow the instructions on how to correctly use the pipet. It is very important to measure the solutions accurately to get the best results. If your absorbance values aren't right, you will have to repeat the procedure, so take your time and make sure you are dispensing the solutions correctly. (**\*Note solution #1 does not contain any  $\text{SCN}^-$** )
3. Dilute this solution to exactly 25mL with your DI water bottle and a disposable pipette for the last few drops of water, **by clicking “Click to Add 5.00 mL  $\text{Fe}^{3+}$  Solution to the Volumetric Flask Below”**. The bottom of the meniscus should touch the volume line. Cap the flask, or cover with parafilm, and mix thoroughly.
4. Pour the mixed solution into a clean 13×100 test tube about  $\frac{3}{4}$  full, label with the standard solution number, and place in the test tube rack. Pour the excess solution in a waste beaker and rinse the flask once with DI water.

- Repeat steps 2-4 for the remaining standard solutions. Solutions #2-5 contain different volumes of  $\text{SCN}^-$ , so measure carefully and remember to change the pipette tip for dispensing each solution so that you make sure that you do not cross-contaminate the reagents.
  - When all the solutions are prepared, take them to a spectrophotometer station. Check to make sure that the spectrophotometer is set to absorb at 445nm.
  - Auto-zero the instrument by filling a clean test tube  $\frac{3}{4}$  full with DI  $\text{H}_2\text{O}$ . Make sure the test tube isn't scratched on the surface and wipe the outside with a tissue before inserting.
  - Close the cover and press the "measure blank" button to zero the instrument.
  - Remove the blank and insert solution #1. Close the cover and record the measured absorbance on your data sheet. You don't need to press a button, **To Measure the absorbance, click on "Click to Measure"**, the value will automatically display on the screen of the spectrophotometer. Record the measured absorbance on your data sheet.
  - Remove solution #1 and repeat with the remaining solutions. You do not need to measure the blank (DI) in between standard solutions.
  - When you are finished collecting absorbance data, ask your instructor to check the absorbance values for each standard solution.
  - Discard all chemical solutions into the waste beaker and clean up the spectrophotometer station so it is ready for the next group.
  - Calculate the concentration of  $\text{Fe}^{3+}$ ,  $\text{SCN}^-$ , &  $\text{FeSCN}^{2+}$  in each of the standard solutions, using the dilution equation  $M_1V_1 = M_2V_2$ .  
(Remember, the final volume of each solution is 25mL.)
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In Part A, the amount of  $\text{Fe}^{3+}$  is 100 fold higher than  $\text{SCN}^-$ , therefore we can assume that this reaction goes "to completion." Effectively, this means that the moles of  $\text{FeSCN}^{2+}$  produced are equal to the initial moles of the  $\text{SCN}^-$  since it was all consumed during the reaction. This does not hold true for Part B of this lab where the  $\text{Fe}^{3+}$  and  $\text{SCN}^-$  are in similar concentrations.

Both  $\text{Fe}^{3+}$  and  $\text{FeSCN}^{2+}$  absorb light in the 430-490nm region of the visible spectrum, so the absorbance of  $\text{Fe}^{3+}$  must be subtracted from each solution in order to determine the absorbance resulting only from the  $\text{FeSCN}^{2+}$ .

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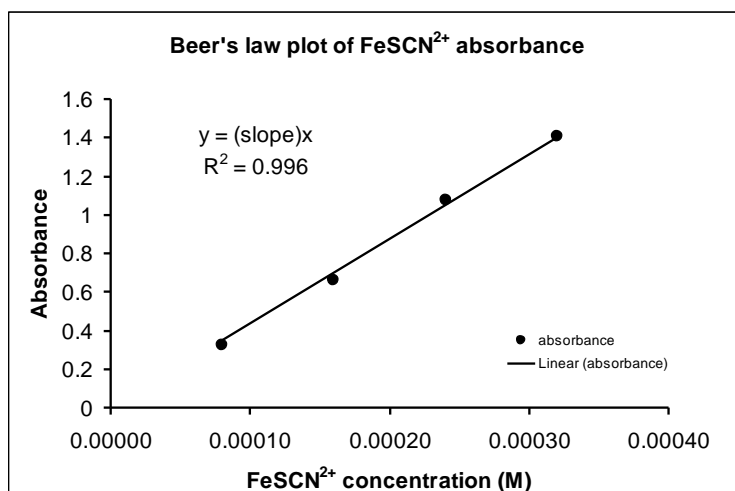
- Subtract the absorbance value for standard solution #1 (in which there is only  $\text{Fe}^{3+}$ ) from each of the standard solutions and record the value in the adjusted absorbance column in the data sheet.
- Plot the Beer's Law Calibration using Excel. If you are unsure how to graph using Excel, make sure that you see your instructor before leaving the lab for a demonstration. The instructions for graphing with excel are as follows:

**Excel Graph:**

- Enter the adjusted absorbance and  $\text{FeSCN}^{2+}$  concentration data in an excel spreadsheet.
- Select chart wizard.
- Select XY scatter plot (without the data connection lines)

- Select data series and select the data to be plotted – The x-axis is the independent variable data (concentration of  $\text{FeSCN}^{2+}$ ). The y-axis is the dependent variable data (adjusted absorbance values).
- Title the graph and label both axes with units as shown below
- Generate the graph as a new sheet.
- Show the linear equation on the graph: Right click on any data point.  
 Add trendline (select linear)  
 Options – Set intercept = 0  
 Display equation on chart
- The regression equation for the line will look like  $y = (\text{slope})x$ . The “slope” should be a rather large number in the thousands. This regression equation is the main objective of the calibration curve since it will allow you to determine the equilibrium  $\text{FeSCN}^{2+}$  concentration for any measured absorbance.
- Print the graph and staple it to your report.

An example of a Beer’s Law graph for this lab is shown below, so your graph should look very similar. The numerical value of the slope has been removed in this graph; you will need to determine the slope based on your data!



## Part B – Determination of the Equilibrium Constant

Go to <https://www.public.asu.edu/~jhwang43/>

Click on “General Chemistry II Laboratory Exercises, By Thomas Cahill”

Click on “Lab4: Determination of an Equilibrium Constant”

Click on “Part B: Determination of the Equilibrium Constant:”

- Prepare the 3 equilibrium solutions as follows:

Solution #	Volume 0.002M Fe <sup>3+</sup>	Volume 0.002M SCN <sup>-</sup>	Total volume (Dilute w/DI)
1	5.00 mL	2.00 mL	10 mL
2	5.00 mL	3.00 mL	10 mL
3	5.00 mL	4.00 mL	10 mL

1. Prepare a 100x dilution of the stock 0.2M Fe<sup>3+</sup> solution by dispensing 1.0 mL of the 0.2M Fe<sup>3+</sup> solution using the auto-pipetter into a **clean** 100 mL volumetric flask, **by clicking “Click to Add 1.00 mL 0.2M Fe<sup>3+</sup> Solution to the 100 mL Volumetric Flask Below”**. Dilute to exactly the 100 mL mark with DI water, **by clicking “Click to Add DI Water to Have a Total 100mL in the left Volumetric Flask”**. Mix the solution thoroughly by inverting and shaking. Pour about 20 mL into a clean 100 mL beaker and label with the new concentration (0.002M Fe<sup>3+</sup>).
2. Attach a **new** pipet tip to the auto-pipetter for dispensing the new concentration of Fe<sup>3+</sup>. Measure the allocated amount of **0.002 M** Fe<sup>3+</sup> for solution #1 and add it to a 10 mL volumetric flask, **by clicking “Click to Add 5.00 mL Fe<sup>3+</sup> Solution to the Volumetric Flask Below”**. It is very important that you measure correctly.
3. Change the pipette tip for SCN<sup>-</sup> and add the amount of SCN<sup>-</sup> for solution #1 to the 10 mL flask, **by clicking “Click to Add 2.00 mL of 0.002 M SCN<sup>-</sup> to the Volumetric Flask Below”**.
4. Dilute this solution very carefully to 10 mL with DI H<sub>2</sub>O, **by clicking “Click to Add DI Water to Have a Total 10mL in the Volumetric Flask Below”**. Cap the flask and mix thoroughly.
5. Pour the solution into a clean 13×100 test tube, label with the solution number and set it aside.
6. Rinse the flask once with DI water and repeat steps 2-6 to prepare the remaining solutions.  
*\*Again, make sure to remember to change the pipette tip for dispensing different solutions\**
7. When all the solutions are prepared, take them to a spectrophotometer station. Check to make sure that the spectrophotometer is set to absorb at 445 nm.
8. Auto-zero the instrument by filling a test tube  $\frac{3}{4}$  full with DI H<sub>2</sub>O. Make sure the tube isn't scratched on the surface and wipe the outside with a tissue before inserting. Close the cover and press the “measure blank” button to zero the instrument.
16. Remove the blank and insert solution #1. Close the cover and record the measured absorbance on the data sheet. You don't need to press a button, the value will automatically display on the screen.

**To Measure the absorbance, click on “Click to Measure”,** the value will automatically display on the screen of the spectrophotometer. Record the measured absorbance on your data sheet.

9. Remove solution #1 and repeat with the remaining solutions. You do not need to measure the blank (DI) in between standard solutions.
10. Have your instructor check the absorbance values for each solution. If your absorbance values aren't right, you will need to repeat the procedure, so take your time and make sure you are dispensing the solutions correctly.
11. When you are finished collecting absorbance data for all the standard solutions, discard all chemical solutions into the designated waste container and clean up the spectrophotometer station so it is ready for the next group.
12. Clean all your equipment and make sure your station is ready for the next group of students. Dispose of the pipet tips in the glass disposal box.
13. Calculate the equilibrium concentration of the  $\text{FeSCN}^{2+}$  complex in each solution using the slope from the Beer's Law calibration curve from Part A. ( $A = abC$ )
14. Calculate the initial concentrations of  $\text{Fe}^{3+}$  and  $\text{SCN}^-$  in each solution.
15. Calculate the equilibrium concentrations of  $\text{Fe}^{3+}$  and  $\text{SCN}^-$  in each solution. (Example 2)
16. Write the equilibrium constant expression for the reaction. (Example 2)
17. Calculate the equilibrium constant ( $K_{eq}$ ) for each solution. (Example 2)
18. Calculate the average equilibrium constant.
19. Calculate the standard deviation for your data.

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### Equilibrium Constant Lab Data

#### Part A – Calibration Curve

Concentration Stock Solution  $\text{Fe}^{3+}$  \_\_\_\_\_

Concentration Stock Solution  $\text{SCN}^-$  \_\_\_\_\_

Standard Solution	Volume $\text{Fe}^{3+}$ (mL)	Volume $\text{SCN}^-$ (mL)	Total Volume (mL)	Initial $[\text{Fe}^{3+}]$ (mol/L)	Initial $[\text{SCN}^-]$ (mol/L)	Equilibrium $[\text{FeSCN}^{2+}]$ (mol/L)	Measured Absorbance	Adjusted Absorbance <sup>a</sup>
1	5.0	0	25.00		0	0		
2	5.0	1.0	25.00					
3	5.0	2.0	25.00					
4	5.0	3.0	25.00					
5	5.0	4.0	25.00					

<sup>a</sup> Absorbance for Sol. 2-5 calculated by subtracting Sol. 1 absorbance due to excess  $\text{Fe}^{3+}$  measured

<sup>b</sup> Remember, we can assume equilibrium moles of  $\text{FeSCN}^{2+}$  are equal to the initial moles of  $\text{SCN}^-$  since  $\text{Fe}^{3+}$  is present in vast excess that forces the reaction to go to completion.

(Show one example calculation for full credit)

- Concentration  $\text{Fe}^{3+}$  in solution:
  
  
  
  
  
  
  
  
  
  
- Concentration  $\text{SCN}^-$  in solution: for solution #2
  
  
  
  
  
  
  
  
  
  
- Concentration  $\text{FeSCN}^{2+}$  in solution: for solution #2

Slope of Beer's Law Plot: \_\_\_\_\_

#### Attach your graph to the lab report for full credit.

Be sure to include a title, axes labels and regression equation.

Also, make sure your graph looks similar to the example graph presented in the lab protocol section.  
\_\_\_\_\_ of 6 pts



## Part B – Equilibrium Constant Determination

Equilibrium solution reagents:

Concentration of  $\text{Fe}^{3+}$  \_\_\_\_\_  
 Concentration  $\text{SCN}^-$  \_\_\_\_\_

Solution #	Volume $\text{Fe}^{3+}$	Volume $\text{SCN}^-$	Total volume	Initial $[\text{Fe}^{3+}]$ mol/L	Initial $[\text{SCN}^-]$ mol/L	Absorbance	Equilibrium $[\text{FeSCN}^{2+}]$ mol/L
1	5.00mL	2.00mL	10.00mL				
2	5.00mL	3.00mL	10.00mL				
3	5.00mL	4.00mL	10.00mL				

(Show your work for full credit )

- Initial Concentration  $\text{Fe}^{3+}$ :
- Initial Concentration  $\text{SCN}^-$  in solution #1:
- Equilibrium Concentration  $\text{FeSCN}^{2+}$  in solution #1:  
 (use slope from Beer's Law Plot and equation on page 1)

Calculate the equilibrium concentrations of  $\text{Fe}^{3+}$  and  $\text{SCN}^-$

Solution #1	$[\text{Fe}^{3+}]$	$[\text{SCN}^-]$	$[\text{FeSCN}^{2+}]$
Initial Concentration			
Change in Concentration			
Equilibrium Concentration			
Solution #2	$[\text{Fe}^{3+}]$	$[\text{SCN}^-]$	$[\text{FeSCN}^{2+}]$
Initial			
Change			
Equilibrium			
Solution #3	$[\text{Fe}^{3+}]$	$[\text{SCN}^-]$	$[\text{FeSCN}^{2+}]$
Initial			
Change			
Equilibrium			

\_\_\_\_\_ of 6 pts

- Write the equilibrium constant expression ( $K_{eq}$ ) for the reaction:

- Calculate  $K_{eq}$  for each solution:

Solution #1 \_\_\_\_\_

Solution #2 \_\_\_\_\_

Solution #3 \_\_\_\_\_

- Calculate the average  $K_{eq}$  for the reaction: \_\_\_\_\_

- Calculate the Standard Deviation = \_\_\_\_\_

$$\sqrt{\frac{\sum_i |x_i - \mu|^2}{n - 1}}$$

**where :**  $\chi_i$  = value of each measurement  
 $\mu$  = average value of all measurements  
 $n$  = number of data points

\_\_\_\_\_ of 4 pts

## POST LAB QUESTIONS

1. Why is a calibration curve constructed?
2. The slope of a Beers Law plot at 445 nm for the absorbing species  $[\text{FeSCN}^{2+}]$  is  $4100 \text{ M}^{-1}$ . If one of the equilibrium mixtures has an absorbance due only to  $[\text{FeSCN}^{2+}]$  of 0.310 what is the concentration of  $[\text{FeSCN}^{2+}]$  in this mixture?
3. Calculate the concentration of  $\text{Fe}^{3+}$  in solution, if 5.00 mL of 0.20M  $\text{Fe}(\text{NO}_3)_3$  was dispensed into a 50.0 mL volumetric flask and diluted with DI to the 50 mL mark.
4. Write the equilibrium constant expressions for the following reactions
  - (a)  $\text{CH}_3\text{CO}_2\text{H} (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{CO}_2^- (aq)$
  - (b)  $\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{-2}(aq)$
5. If the  $K_{eq}$  value for (a) above was 14 would you expect there to be more reactants or products?
6. Determine the pressure-based  $K_{eq}$  for the reaction:  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$   
given that  $1.00 \times 10^{-2}$  moles of  $\text{SO}_2$  and  $2.00 \times 10^{-2}$  moles of  $\text{O}_2$  were initially placed in a 2.00 L reaction chamber. The chamber contained  $7.5 \times 10^{-3}$  moles of  $\text{SO}_3$  when equilibrium was established at 727 °C. Since you need to calculate the pressure-based equilibrium constant, you will need to use the ideal gas equation ( $PV=nRT$ ) to convert the moles of gas into pressure with units of atmospheres. (remember that one formulation of R is 0.0821 L·atm/mol·K)

Total \_\_\_\_\_ of 6 pts  
\_\_\_\_\_ of 25 pts