Experiment 12C

12/18/2018

THERMODYNAMIC PROPERTIES OF AMMONIUM CARBAMATE[1]

MATERIALS: Ammonium carbamate apparatus.

PURPOSE: The purpose of this experiment is to calculate the equilibrium constant, K_p, for a chemical reaction at several temperatures and to use these values to calculate the thermodynamic properties of the reaction.

LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Derive an equation relating partial pressures of gaseous reactants and products to the equilibrium constant for a reaction.
2. Determine $\Delta_r G°$, $\Delta_r H°$ and $\Delta_r S°$ for a reaction from the values of the equilibrium constant at several temperatures.
3. Determine the $\Delta_f G°$ for a reactant from $\Delta_r G°$ for a reaction and the tabulated values of $\Delta_f G°$ for the products of the reaction.
4. Explain the correlation between $\Delta_r G°$ for a reaction and spontaneity under a given set of experimental conditions.

DISCUSSION:

The change in Gibbs free energy of a chemical reaction, $\Delta_r G$, is the criterion that is used to indicate whether or not the reaction is spontaneous. $\Delta_r G$ is related to the enthalpy change of reaction, $\Delta_r H$, and the entropy change of reaction, $\Delta_r S$, by the expression $\Delta_r G = \Delta_r H - T\Delta_r S$, where T is the Kelvin temperature. Knowledge of the thermodynamic quantities associated with a chemical reaction is important since experimental conditions, especially temperature, can sometimes be manipulated to cause the reaction to occur in the desired direction.

For example, in a closed atmosphere, such as in submarines and space vehicles, control of the carbon dioxide level is crucial. Normal air contains a very small quantity of carbon dioxide, approximately 0.03% by volume. But high levels of carbon dioxide are toxic. The average person produces 120 g of CO_2 per day at normal activity levels. This amount increases as the activity level increases. High carbon dioxide concentrations, measured as the partial pressure of CO_2 (P_{CO2}), can cause impaired judgment, dizziness, loss of muscular coordination, unconsciousness, and eventually death. For this reason, methods of removing carbon dioxide are of great interest to the military. For more information on carbon dioxide toxicity and removal methods, consult the *Naval Applications of Chemistry* website, at the link for submarine air treatment.[2]

Early NASA spacecraft used non-regenerative carbon dioxide scrubbers such as lithium hydroxide. They remove carbon dioxide by the spontaneous chemical reaction indicated by the following equation:

$$CO_2\,(g) + 2\,LiOH\,(s) \rightarrow Li_2CO_3\,(s) + H_2O\,(g) \qquad (1)$$

Sufficient lithium hydroxide must be carried on board the spacecraft to absorb the carbon dioxide produced during the entire flight. Assuming 100% efficiency of scrubbing, 130 g or 5.5 moles of lithium hydroxide are needed per day per crew member.

[1] Joncich, M.J., Solka, B.H., Bower, J.E., *J. Chem. Ed.*, **1967,** *44*, 598. Bennett, R.N., et al., *Trans. Faraday Soc.*, **1953**, *49*, 925.

[2] http://intranet.usna.edu/ChemDept/_files/documents/navapps/ADDITIONAL-INFO/Submarine%20Air/SUBMARINE%20AIR%20TREATMENT_2010.pdf

On a submarine, which must stay submerged for extended periods of time, carrying enough lithium hydroxide to remove all of the carbon dioxide produced by the crew would require too much space and weigh too much[3]. Instead, submarines use a regenerative scrubbing system. This regenerative system is based upon the chemical reaction between monoethanolamine (MEA) and carbon dioxide shown in the equation below.

$$HOCH_2CH_2NH_2\ (aq) + CO_2\ (g) \leftrightarrows HOCH_2CH_2NHCOOH\ (aq) \qquad (2)$$

The position of equilibrium for this reaction can be controlled by changing the temperature. At low temperatures and relatively high carbon dioxide pressures, carbon dioxide is absorbed because the forward reaction is spontaneous. At higher temperatures and low carbon dioxide pressures, carbon dioxide is produced because the reverse reaction is spontaneous. An exchange system is used which allows for removal of between 70% and 90% of the carbon dioxide from the crew air spaces. The waste carbon dioxide is collected and pumped overboard.

The purpose of this experiment is to study a system similar to the MEA/CO_2 system, the ammonium carbamate system. Ammonia, like MEA, reacts with carbon dioxide to form a carbamic acid (H_2NCO_2H). The carbamic acid then reacts with a second ammonia molecule to form a carbamate salt, ammonium carbamate ($NH_4CO_2NH_2$).

$$CO_2\ (g) + NH_3\ (g) \leftrightarrows H_2NCO_2H\ (s) \qquad (3)$$

$$H_2NCO_2H\ (s) + NH_3\ (g) \leftrightarrows NH_4CO_2NH_2\ (s) \qquad (4)$$

The overall reaction is:

$$CO_2\ (g) + 2\ NH_3\ (g) \leftrightarrows NH_4CO_2NH_2\ (s) \qquad (5)$$

In this experiment the thermodynamic properties of the reverse reaction, the decomposition of ammonium carbamate, will be determined by measuring the equilibrium vapor pressure as a function of temperature. Ammonium carbamate decomposes to form carbon dioxide and ammonia as shown in the equation below.

$$NH_4CO_2NH_2\ (s) \leftrightarrows 2\ NH_3\ (g) + CO_2\ (g) \qquad (6)$$

The thermodynamic properties of a reaction can be determined from equilibrium constants for the reaction at several temperatures. These values are related by the equation

$$\ln K_P = -\frac{\Delta_r H^\circ}{R}\frac{1}{T} + \frac{\Delta_r S^\circ}{R} \qquad (7)$$

where K_P is the equilibrium constant. This assumes that $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are constant over the entire temperature range. Since this equation has the form of the equation for a straight line, y = mx + b, the slope and intercept of a plot of ln K_P versus 1/T can be used to calculate values for $\Delta_r H^\circ$ and $\Delta_r S^\circ$. The desired thermodynamic information for a reaction and its components can be calculated from this equation, other basic equations of thermodynamics, and experimental data.

A word on units.
Note that the units of the slope in equation 7 are determined from the 1/T term only because K_P is unit-less. Also, when determining the slope $\Delta y/\Delta x$, the Δy part is the change in ln K_P. This change between any two points, ln K_{P2} – ln K_{P1}, can also be written as ln (K_{P2}/K_{P1}). It can be seen that even if K_P had units, the K_P units would cancel in the slope expression.

PROCEDURE:

See pre-lab. Experimental data must be collected **the week before** the lab is scheduled. A diagram and picture of the apparatus are shown on the next page.

[3] For a three month cruise, the submarine would have to carry about 13 kilograms of lithium hydroxide per person or 1.4 tons for a 100 person crew. This would require about 602 L or 23 ft^3 of space.

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Partner _____________________________ Date ________________________

DATA SECTION
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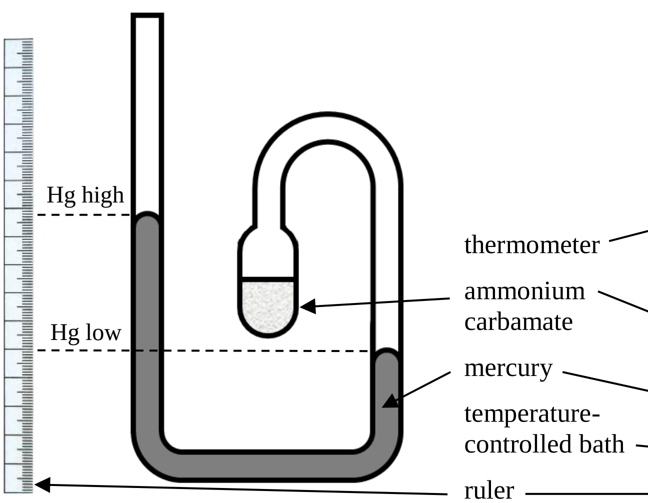
Table 1 - Data for the Reaction: $NH_4CO_2NH_2$ (s) ⇆ 2 NH_3 (g) + CO_2 (g)			
Reading	Temperature (°C)	Hg height (cm) high	Hg height (cm) low
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			



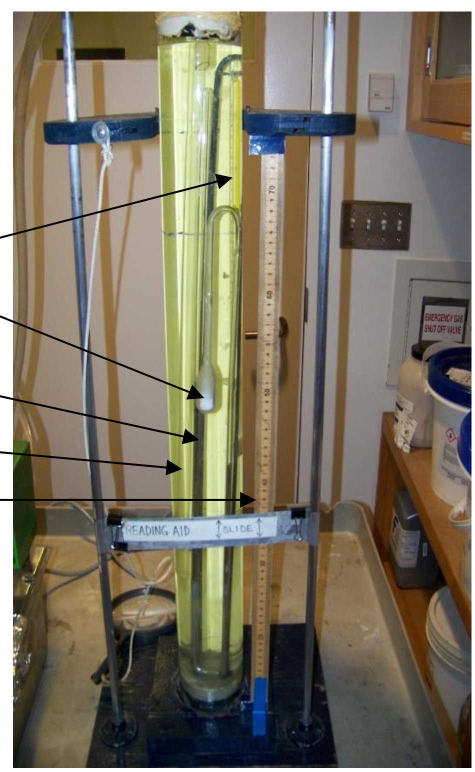


Figure 1. Figure and picture of apparatus. The closed-end mercury manometer is contained in a temperature-controlled bath. There is a ruler for measuring the heights of the mercury, and a thermometer for measuring the temperature of the bath (and manometer). Hg "high" and Hg "low" refer to the measured heights on the "left" and right" side of the manometer, respectively.

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Partner _____________________________________ Date _______________________________

DATA TREATMENT
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Part A: Graphing your Data

Prepare this spreadsheet and graph after you have collected the data. Complete the graph by the date specified by your instructor.

1. Enter your experimental values from the DATA SECTION into a spreadsheet program in order of increasing temperature (°C).

2. Use the spreadsheet program to calculate the following values for each set of data:

   a. Temperature in Kelvin, T. Note: Add 273.15 to the temperature in °C.
   b. 1/T (K^{-1})
   c. The difference in the heights of the mercury columns in cm, Δh. (This is the equilibrium pressure in cm Hg.)
   d. The equilibrium pressure in atm, P_{eq}. Note that this is the total pressure, P_{total}.

   By entering the appropriate equations, the spreadsheet program will compute the values for these items.
   Do not calculate the values on a calculator and merely type the results into the spreadsheet. Use Excel formulas. Label your spreadsheet clearly and format it properly.

3. Write the equation for K_P derived in the pre-lab.

4. Using P_{eq} (in atm) and the equation above, use your spreadsheet to compute the value of K_P at each temperature. Note: $P_{eq} = P_{total}$.

5. Calculate ln K_P and $\Delta_r G°$ for each temperature. To make it clear that $\Delta_r G°$ does vary with temperature, the temperature is indicated by writing the Gibbs free energy change as $\Delta_r G°_T$.

6. Construct a graph of ln K_P versus 1/T and determine the slope and intercept of the line by performing a linear regression (i.e., trendline). Label this graph properly and submit it with your lab report. Your final graph should include a descriptive title, axes labels and units, regression line, equation for the regression line, and the R^2 value.

   slope of line: ____________________________ units for the slope = ___________

   y-intercept: ____________________________

   R^2 value: ______________________________

Part B: Calculating Thermodynamic Functions

1. Using the results from your ln K_P vs. 1/T graph, calculate the value for $\Delta_r H°$. Show your work. It is assumed that over the small temperature range of this experiment, $\Delta_r H°$ is independent of temperature. Calculation of $\Delta_r H°$ from the slope of your line is therefore valid. R = 8.314 J/mol·K

$\Delta_r H°$ = ______________________ kJ/mol

2. Using the values of the slope and the y-intercept, calculate the value of K_P at 298.15 K.

$K_{P,\ 298.15}$ = __________________________

3. Calculate the value of $\Delta_r G°_{298.15}$ using your value for the equilibrium constant K_P at 298.15 K.

$\Delta_r G°_{298.15}$ = ______________________ kJ/mol

4. Using your experimentally determined values of $\Delta_r H°$ and $\Delta_r G°_{298.15}$, calculate $\Delta_r S°$. The value of $\Delta_r S°$ is also assumed to be constant over the experimental temperature range.

$\Delta_r S°$ = ______________________ J/K·mol

5. Calculate the change in the internal energy for the reaction, $\Delta_r U°$, at 298.15 K from your value of $\Delta_r H°$.

$\Delta_r U° = \Delta_r H° - (\Delta n)RT$ where Δn = the change in the total moles of gas (from balanced chemical equation).

$\Delta_r U°$ = ________________________ kJ/mol

6. The thermodynamic quantities calculated to this point ($\Delta_r H°$, $\Delta_r G°_{298.15}$, $\Delta_r S°$ and $\Delta_r U°$) are measures of the changes in the enthalpy, Gibbs free energy, entropy, and energy, respectively, at 298.15 K and standard state for the overall reaction. Tabulated values of the standard heats of formation ($\Delta_f H°$), standard free energies of formation ($\Delta_f G°$), and the standard molar entropies (S°) for NH_3 (g) and CO_2 (g) are available in your textbook and in the *Handbook of Chemistry and Physics*. By combining the overall thermodynamic reaction quantities with the specific quantities for NH_3 and CO_2, it is possible to evaluate the standard heat of formation ($\Delta_f H°$), standard free energy of formation ($\Delta_f G°$), and the standard molar entropy (S°) for ammonium carbamate.

a. Consult your textbook, Kotz et al, Appendix L, for the thermodynamic quantities for NH_3 (g) and CO_2 (g) at 298.15 K. Fill in the table below, using all significant figures from Appendix L.

Data Treatment Table 1

Compound	$\Delta_f H°_{298.15}$ (kJ/mol)	$\Delta_f G°_{298.15}$ (kJ/mol)	$S°_{298.15}$ (J/K·mol)
NH_3 (g)			
CO_2 (g)			

Use the thermodynamics values you calculated for the *overall reaction* ($\Delta_r H°$, $\Delta_r G°_{298.15}$, $\Delta_r S°$) and the values from Data Treatment Table 1 (values for the *individual* components of *NH_3* and *CO_2*) to determine the thermodynamic quantities for *ammonium carbamate alone* in questions b, c, and d below.

b. Calculate the value of $\Delta_f H°$ for $NH_4CO_2NH_2$ at 298.15 K.

$\Delta_f H°$ = _________________________ kJ/mol

c. Calculate the value of $\Delta_f G°$ for $NH_4CO_2NH_2$ at 298.15 K.

$\Delta_f G°$ = ________________________ kJ/mol

d. Calculate the value of S° for $NH_4CO_2NH_2$ at 298.15 K.

S° = _________________________ J/K·mol

QUESTIONS
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1. List the values you calculated for the reaction for the decomposition of ammonium carbamate. Include units.

   a. $K_{P,\ 298.15}$ =

   b. $\Delta_r H°$ =

   c. $\Delta_r S°$ =

   d. $\Delta_r G°_{298.15}$ =

2. Write the reaction for the decomposition of ammonium carbamate. Include the physical state of each species.

3. Predict from the chemical equation whether the decomposition of ammonium carbamate is accompanied by an increase or decrease in entropy. Explain your reasoning. Are your results in accordance with your prediction?

4. The calculated value for $\Delta_r G°_{298.15}$ is positive indicating a nonspontaneous reaction, yet under the reaction conditions measured, some decomposition has clearly occurred. Explain why.

5. Is the reaction spontaneous under standard conditions at 298.15 K? As the temperature is increased, will the reaction become spontaneous? Explain.

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Date _______________________________

PRE-LAB EXERCISES
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Complete these exercises by the date specified by your instructor. The Part B exercises below are also on OWL and might have to be completed there. Consult your instructor. If completed on OWL, copy your answer from OWL question 4 into the space available on page 4, question 3, as it will be needed for the Data Treatment.

Part A: Data Collection

1. You must collect the data for this experiment **the week before** the lab is scheduled. The apparatus required for this experiment will be set up daily (Monday – Friday) on the chemistry lab deck between the hours of 0745 and 1530. The temperature of the apparatus will be changed in the morning (before 0745) and at lunch (after 1200) so it is possible to obtain 2 measurements each day.

2. Using the apparatus, carefully **record the temperature** and **the heights of the mercury levels in the manometer** in Table 1 of the DATA SECTION, using the correct number of significant figures and units. It is your responsibility to complete Table 1 by the date set by your instructor.

Part B: Derivation of Equations

1. Write the equilibrium expression, K_P, for the decomposition reaction studied in this experiment.

$NH_4CO_2NH_2\,(s) \leftrightarrows 2\,NH_3\,(g) + CO_2\,(g)$ K_P =

ammonium carbamate

2. In the experimental apparatus, all the gases inside the sealed end were formed from the decomposition of solid ammonium carbamate, as shown above. Applying Dalton's Law of Partial Pressure, what is the expression for the total pressure in the sealed end in terms of the gases present?

P_{total} = ____________ + ______________

3. a. Based on the balanced chemical equation, what is the stoichiometric mole ratio between NH_3 and CO_2?

$NH_3 : CO_2$

_________ : _________

b. Using Dalton's Law of Partial Pressures and the stoichiometric relationship between ammonia and carbon dioxide (and therefore between P_{NH3} and P_{CO2}), what fraction of the total pressure in the tube comes from carbon dioxide? What fraction of the total pressure in the tube comes from ammonia?

NH_3: __________ CO_2: __________

4. Substitute the relationships just derived above into the equation for K_P so that K_P is given in terms of only the total pressure, P_{total}, rather than the partial pressures of ammonia and carbon dioxide. This equation is needed on page 4, #3.