

A PROPOSAL TO THE AMERICAN VACUUM SOCIETY

FOR AN EXPERIMENT TO

DETERMINE THE EQUILIBRIUM CONSTANT AND

THE HEAT OF REACTION

IN AN EQUILIBRIUM SYSTEM

SUBMITTED BY

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Determination of an Equilibrium Constant, K_p , and Heat of Reaction

ABSTRACT

This proposal is intended to present a method by which high school chemistry students or at least Advanced Placement chemistry students can determine the equilibrium constant for a reaction involving gases. The proposal is to collect data at two different temperatures and then make appropriate calculations to determine the Heat of Reaction and the equilibrium constant. At the end of the paper another method for determining the heat of reaction is discussed.

The proposal is to introduce into an evacuated flask whose temperature is known, a sample of solid reagent. Solids are to be chosen based on the fact that they are known to decompose into gaseous products at reasonable temperatures and pressures. Since the flask is evacuated to begin the experiment, any subsequent pressure that develops will be due to formation of the product gases. If a sufficient amount of the solid is placed in the flask, the system will reach equilibrium. The total pressure in the flask is to be monitored until the pressure reaches and maintains a maximum value. The reaction will be at equilibrium at this time. Knowing the total pressure at equilibrium and using the reaction stoichiometry, one can calculate the individual pressures of the product gases and thus the equilibrium constant.

The equilibrium constant can be determined at two different temperatures by immersing the flask in an ice bath and then again in a container of boiling water. Application of the van't Hoff equation will produce a value for the Heat of Reaction

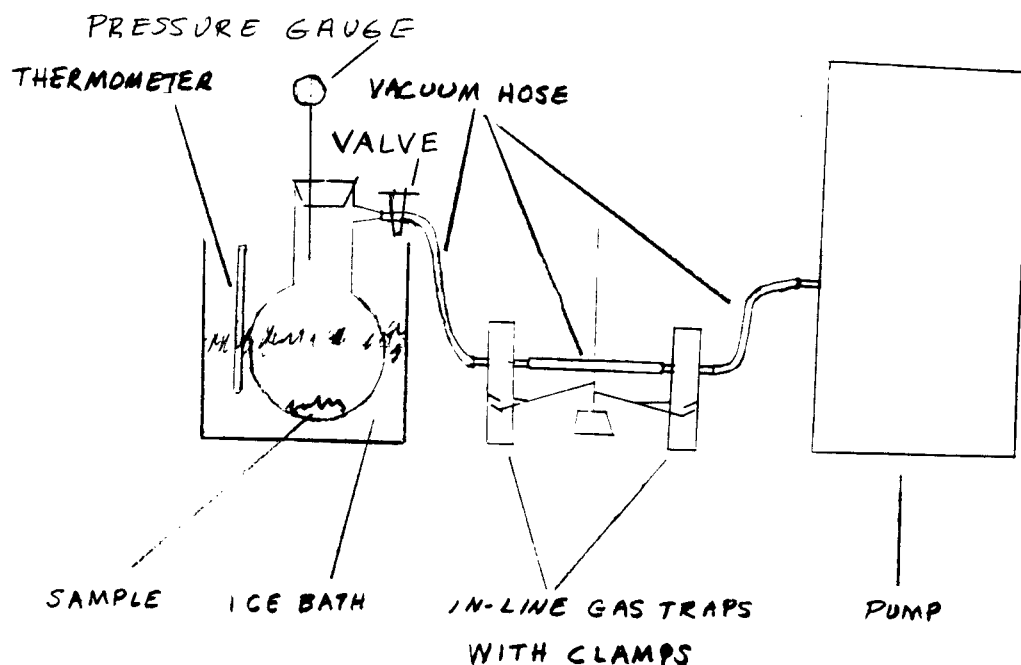
PROPOSAL

EQUIPMENT: High quality vacuum pump; gauge and stopcock assembly, accurate thermometer; filter flask and stopper; 2 large beakers; hot plate; vacuum hose; hydrogen sulfide trap; ammonia trap; ice; pressure gauge; valve

REAGENTS: 1.0 gram Ammonium bisulfide

DATA: The following data are to be measured and recorded:

The equilibrium temperature of the ice bath,
The pressure within the flask while it is in the ice bath,
The equilibrium temperature of the boiling water bath,
The pressure within the flask while it is in the boiling bath



EXPERIMENTAL:

- 1 Assemble the apparatus as shown in the apparatus sketch. For this experiment, the H_2S and NH_3 filters are to be in place.

- 2 Close the valve and place the sample of NH_4HS in the flask.
- 3 Stopper the flask securely. and verify that all connections are tight.
- 4 Place a mixture of ice and water in the large beaker.
- 5 Place the flask in the beaker so that it is mostly submerged.
- 6 Gently stir the ice-water mixture and monitor its temperature near the flask.
- 7 When the temperature has stabilized, allow a few minutes for the flask to reach temperature equilibrium with the water bath. Record this temperature.
- 8 Open the valve and start the vacuum pump to evacuate the flask.
- 9 Monitor the pressure and when it reaches a minimum, stop the pump and close the valve. Disconnect the valve and flask from the hose leading to the trap, keeping the valve closed at all times.
- 10 Monitor the pressure.
- 11 When the pressure becomes constant, record its value, and then place the flask in a warm water bath and bring the water to boil.
- 12 Monitor the temperature and record its maximum value.
- 13 Monitor the pressure until it becomes constant. Record this pressure.
- 14 Remove the flask from the water bath, detach the hose, and place the flask in a fume hood or appropriate storage bag.

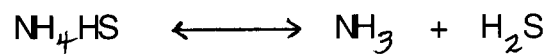
PRELIMINARY REPORT

DATE_____ NAME_____

- 1 Explain why NH_4HS does not appear in the equilibrium expression.
- 2 If no solid remains when the pressure reaches a maximum, what effect will this have on the experiment and the calculations? Why?
- 3 Why is the flask evacuated with the sample present?
- 4 Given that the value for K_p for this reaction was found to be .367 at 50 C, what is the pressure of the NH_3 at this temperature?

CALCULATIONS:

The equation for the reaction is:



- 1 Making use of the fact that the pressure of the NH_3 equals the pressure of the H_2S which equals 1/2 the total pressure, calculate K_p for the reaction at each temperature, where

$$K_p = P_{\text{NH}_3} \times P_{\text{H}_2\text{S}}$$

- 2 Using the van't Hoff equation, as follows, calculate the Heat of Reaction for ammonium bisulfide.

$$\frac{\log K_{p2}}{\log K_{p1}} = - \frac{\Delta H}{2.303R} \left(\frac{T_2 - T_1}{T_2 T_1} \right)$$

- 3 Using a handbook, find the accepted value for the Heat of Reaction and calculate the % error in the experimental value.
- 4 List possible sources of error and how they may have affected the experimental value.

NOTES AND DISCUSSION

The van't Hoff equation may be expressed in many forms. The form used here is the integrated form : $\log K_p = \frac{-\Delta H}{2.303RT} + C$

where K_p is the equilibrium constant for the reaction at the Kelvin temperature, T . H is the heat of reaction which may be considered constant over the temperature ranges of this experiment. R is the universal gas constant expressed in Joules/K-mole and C is an integration constant. If K_p data can be generated at several temperatures, a plot of $\log K_p$ vs $1/T$ will yield a straight line whose slope will be equal to

$$\frac{-\Delta H}{2.303R}$$

Thus one can solve this equation and determine H . A possible method for obtaining this data is discussed at the end of these comments.

This experiment involves the "two point" form of the van't Hoff equation :

$$\frac{\log K_{p2}}{K_{p1}} = \frac{\Delta H}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

This form may be derived as follows: suppose at a given temperature, T_1 , the equilibrium constant is determined to be K_{p1} , and then again at another temperature, T_2 , the constant is found to be K_{p2} . If each set of values is inserted into the van't Hoff equation, 2 equations are generated:

$$\begin{aligned} \log K_{p1} &= -\Delta H/2.303RT_1 + C \quad \text{and} \\ \log K_{p2} &= -\Delta H/2.303RT_2 + C \end{aligned}$$

Subtracting equation 1 from equation 2 and rearranging terms yields the two-point form. Two relatively easy temperatures to achieve and maintain have been chosen--the freezing and boiling points of water.

Safety is of some concern in this experiment. Total pressures in excess of 3 atmospheres will be reached at the boiling point of water. Good quality glassware that has not been damaged or fatigued should be used. A shock

resistant safety shield placed between the audience and the experiment may be an option to consider. The toxic gases can successfully be removed from the system using molecular sieves. The products listed have been determined to be sufficient for this; there are certain to be other products which also will serve this purpose.

Thermodynamic data yield values for the Heat of reaction of +98.5Kj (Glasstone and Lewis) and +96.6 Kj (McQuarrie and Rock; CRC Handbook)

A preliminary report for the student has been included. This should be completed prior to the student attempting the experiment.

A different approach to determining Heat of Reaction may be taken. This would involve placing a sample of ammonium bisulfide in the flask, bringing it to equilibrium at the boiling point of water, and recording the pressure. Then the flask is allowed to cool slowly (to ensure that gases and solid are in equilibrium) and temperature/pressure readings made every few degrees of temperature change. After the collection of several data points--at least 10--the data can be plotted to determine ΔH . K_p must be calculated at each temperature then a plot of $\log K_p$ vs $1/T$ will yield a straight line whose slope is equal to $-\Delta H/2.303R$

BUDGET:

Vendor: VWR Scientific Products

Gauge and stopcock assembly	87.89
Hot plate	105.00
Filter flask	30.00
Vacuum hose	18.95
Vacuum pump	1210.00
Valve	20.00
Pressure gauge	80.00
	1551.84

Vendor: Fisher

Large Beakers (2 @ 40.42)	80.84
Digital thermometer	139.95
Equipment for H ₂ S trap	10.00
	230.79

Vendor: SKC Inc.

In-line vapor traps (2)	40.00
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Vendor: GSA Resources Inc.

Sorbent for NH ₃	50.00
Sorbent for H ₂ S	50.00
	100.00

Total cost: 1822.63