Homogeneous Gaseous Equilibrium:
The Dissociation of N_2O_4

Object

In this experiment the degree of dissociation, α, of N_2O_4 is determined at various temperatures by measuring the density of the gas at a known total pressure. From the experimental data, the equilibrium constants and the enthalpy and free energy of dissociation are calculated.

Procedure

Connect the Dumas bulb to a mechanical pump and exhaust to a pressure of 1-2 mbar. Weigh the evacuated bulb to 0.1 mg. Then fill the bulb with dry air at atmospheric pressure by allowing the air to enter through a $CaCl_2$ drying tube. Record the laboratory temperature and the barometric pressure. Close the stopcock and reweigh the bulb. Evacuate the bulb again and reweigh.

Figure 1: Vacuum Line

Working in the hood and under the supervision of the instructor, put some N_2O_4 into the Dumas bulb while cooling the bulb in an ice/salt bath. Stop filling the bulb as soon as you see liquid (colorless) condensing in the bulb. The bulb should eventually be immersed in a 2 L beaker of water regulated to a little below 40˚C with the capillary held vertically above the water.

As soon as the bulb is in the beaker of water, open the stopcock until the liquid N_2O_4 disappears. Then close the stopcock. Raise the temperature to about 40˚C and keep it constant to within 0.10˚ for at least five minutes. Again, vent out the excess NO_2 into the hood. Close the stopcock, in the hood allow bulb to cool and gas to diffuse out of the stem, dry the bulb carefully, and weigh bulb to the nearest 0.1 mg. Read the barometer.

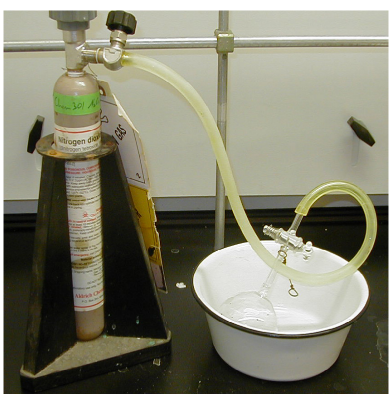

Figure 2: Filling Bulb

Repeat the last procedure for temperatures of 50˚C, 60˚C, 70˚C, and 80˚C, each time holding the temperature constant to 0.1˚C. Then evacuate the remaining gas in the bulb by means of a water aspirator.

Safety

•NO_2 is a strong oxidizer. You don't want to breathe it.
Inhalation hazard copied from a Material Safety Data Sheet (MSDS): Cough, Dizziness, Headache, Sweating, Labored breathing, Nausea, Shortness of breath, Sore throat, Vomiting, Weakness, Wheezing, Symptoms may be delayed.

•The vapor pressure of NO_2 is ~0.96 bar at 20°C. You don't want to heat a closed glass container with liquid NO_2 much above 40°C to avoid over-pressurizing the glass bulb.

Calculations

1. From the weights of the Dumas bulb when evacuated and when filled with dry air and from the average molecular weight of the air, calculate the volume, *V*, of the bulb.

2. From the following formulas calculate α and K_p at the various temperatures.

$$\alpha = \frac{MPV}{mRT} - 1 \qquad\qquad K_p = \frac{4\alpha^2 P}{1-\alpha^2} \qquad (1)$$

   where *M* = molecular weight of undissociated N_2O_4, *P* = the barometric pressure, *V* = volume of bulb, *m* = mass of gas in the bulb, *R* = universal gas constant. (Note, this α is not the thermal coefficient of expansion.)

3. Record your values in a table with the following columns.

$$˚\mathrm{C} \quad T \quad \frac{1}{T} \quad P(\mathrm{atm}) \quad m \quad V \quad \alpha \quad K_p \quad \ln K_p$$

4. Plot ln K_p against $\frac{1}{T}$ in such a way so that you can draw a straight line through the points and extrapolate to 25˚C or calculate K_p (25°C) from the equation for the line fit.

5. From the value of K_p at 25˚ obtain ΔG^0 from $\Delta G^0 = -RT \ln K_p$.

6. From the slope of the curve in part 4, obtain ΔH^0 from *slope* $= -\frac{\Delta H^0}{R}$.

7. Calculate K_C for 25˚C.

Report

1. Derive the formulas given in (2) under Calculations. α is defined in Verhoeck and Daniels [1931]. Note that Verhoeck and Daniels use an unusual definition for $P^{o}_{N_2O_4}$.

2. Include from the previous section the items under (1), (3), (4), (5), (6), (7). Compare literature values for items (5) and (6).

Reference

F. H. Verhoeck and F. Daniels, *J. Am. Chem. Soc*. **53**, 1250 (1931). (On reserve and on Blackboard)