

Homogeneous Gas Phase Equilibrium

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Theory

The molecule N_2O_4 is a dimer which exists in a strongly temperature dependent equilibrium:



Using pressure as our variable and treating the species as ideal gases, we can write the equilibrium constant as

$$K(T) = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}. \quad (2)$$

The equilibrium constant is related to the free energy change for the reaction,

$$\Delta G^\circ = -RT \ln K, \quad (3)$$

and ΔG° , in turn, is related to the enthalpy and entropy changes,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ. \quad (4)$$

We may evaluate ΔH° if we can measure K as a function of T , for we have

$$\frac{\partial \ln K}{\partial (1/T)} = \frac{-\Delta H^\circ}{R}. \quad (5)$$

Measuring K at any temperature gives ΔG° at that temperature, and the slope of a plot of $\ln K$ versus $1/T$ yields ΔH° at that temperature. Once ΔG° and ΔH° are known, ΔS° can easily be found.

Since the number of molecules doubles as reaction (1) proceeds from left to right, we can monitor the extent of the reaction by measuring the total pressure. Suppose we had a bulb of N_2O_4 at temperature, T , and none of it was dissociated; this corresponds to a pressure P_o . Now let the fraction of N_2O_4 dissociated be α . Then the partial pressures of the two species are

$$P_{\text{N}_2\text{O}_4} = P_o(1 - \alpha), \quad (6a)$$

$$P_{\text{NO}_2} = 2\alpha P_o, \quad (6b)$$

and the equilibrium constant is given by

$$K = \frac{(2\alpha P_o)^2}{(1 - \alpha)P_o} = \frac{4\alpha^2 P_o}{(1 - \alpha)}. \quad (7)$$

The total pressure in the system is

$$P_{\text{tot}} = P_{\text{N}_2\text{O}_4} + P_{\text{NO}_2} = P_o(1 + \alpha), \quad (8)$$

and we can determine α from measurement of P alone,

$$\alpha = \frac{P_{\text{tot}}}{P_o} - 1, \quad (9)$$

provided we have some way of measuring P_o separately. This can be done if we can cool the system to some temperature at which dissociation is negligible ($\alpha = 0$, $P = P_o$), or heat it to some temperature at which dissociation is essentially complete ($\alpha = 1$, $P_{\text{tot}} = 2P_o$). Note that P_o is a function of temperature—it is the pressure that would be measured at a given temperature if all the N_2O_4 were undissociated. This pressure, P_o , clearly depends on the temperature. Since we are treating the gases as ideal, we can use the ideal gas laws to refer P_o at one temperature to any other temperature. For example, if we heat the gas to some high temperature, T_h , in order to completely dissociate N_2O_4 and get $P_o(T_h)$, then $P_o(T)$ at any other temperature is given by

$$P_o(T) = P_o(T_h) \frac{T}{T_h}, \quad (10)$$

since the pressure of an ideal gas is directly related to the temperature. Using (10), (9), and (7) we can compute $K(T)$ and hence obtain ΔG° , ΔH° , and ΔS° for the reaction.

Experimental

In this experiment, the temperature of the bulb is controlled by a heating tape connected to a variac. The bulb has already been filled with NO_2 by the instructor. Measure P_{tot} versus T making sure to include measurements at a temperature sufficiently high for complete dissociation. The pressure is measured with a pressure transducer, and the temperature is measured with a thermocouple.

Procedure

Beginning at room temperature, make a series of six to ten T and P readings in increments of $6 - 8^\circ\text{C}$ up to approximately 80°C . Then increase the temperature to $\sim 120^\circ\text{C}$ to determine P_o . Pressure readings should only be recorded when the pressure has stabilized.

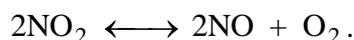
Calculations

Convert the pressure to atmospheres and the temperature to degrees Kelvin. Determine P_o at the highest temperature assuming complete dissociation. Correct P_o to the other temperatures used.

For data recorded between room temperature and 80°C , make a table showing P , α , K , and ΔG° as a function of T . Plot $\ln K$ versus $1/T$ and obtain the least squares straight line fit to your data. Determine ΔH° and ΔS° . Compare with literature values.

Using your value of ΔH° , extrapolate K to the highest temperature recorded for determination of P_o and see if complete dissociation is a valid assumption. How much error is introduced by this assumption?

A possible complication at higher temperatures is the reaction



Using thermodynamic tables, estimate the possible effect of this reaction on your results.