Thermodynamics of the NO_2 - N_2O_4 Equilibrium by FTIR

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Experiment Overview

An understanding of how experimental variables influence the position of equilibrium for a reaction mixture is of fundamental importance to a chemist, biochemist or other molecular scientist. The ability to describe a reaction in terms of its thermodynamic equilibrium constant and hence Gibb's Free Energy and see the relative influences of enthalpic and entropic drivers gives a great deal of information about the processes in the chemical reaction. In addition, these parameters provide the basis for predictive tools to describe how the reaction will proceed under any experimental conditions. For example, a knowledge of the reaction enthalpy enables the temperature dependence of the Free Energy (and *K*) to the determined through the Gibbs-Helmholtz Equation. Although, the equations and concepts underlying thermodynamics are introduced at first year undergraduate level, it is rare to be able to study the thermodynamics of a reaction in detail until subsequent years. This experiment beautifully illustrates the amount of useful information that can be gleaned about the temperature dependence of a reaction in a clear way while ensuring students get good data in a reasonable time frame (ie one lab session).

The equilibrium between NO_2 and N_2O_4 is a classic experiment investigated in a variety of ways, often just to illustrate the perturbing of equilibrium and Le Chatelier's principle in a qualitative fashion. It has normally been studied by measuring pressure as a function of temperature or by UV-Vis spectroscopy. Indeed, one of the authors can remember at school (in less OH&S conscious and encumbered days than now) having Le Chatelier's principle demonstrated via a gas syringe being squeezed and the colour changing as more N_2O_4 was formed.

The experiment presented here is novel in the sense that it uses FTIR spectroscopy to determine the composition of the mixture as a function of temperature. From the changing absorbances for each species the students clearly see how the equilibrium is shifting. The experimental set up has proven to be very robust. We currently use the experiment at second year level. Numerous extensions of the experiment are possible including practice at vacuum filling techniques and more in depth understanding of the spectroscopy side, if the experiment was to be run at a higher level.

The experiment is designed to reinforce to students the basic principles of equilibrium and thermodynamic concepts and related equations. The students obtain the spectra and calculate the corrected absorbance of peaks for NO_2 and N_2O_4 by using the software to correct for background and baseline absorbance. From the absorbances of the species as a function of temperature, they obtain the molar extinction coefficient for N_2O_4 given the value for NO_2. The students are then able to determine the concentration and pressure based equilibrium constants as a function of temperature. This exercise is also designed to give the students practice and experience at setting up spreadsheets. From the van't Hoff isochore plot the value of *K* at 298.15 K is obtained and the standard reaction enthalpy (ΔH^o), together with the uncertainty from the regression analysis. These two values then allow the determination of ΔG^o and ΔS^o together with their respective uncertainties. The experimental values are then compared with those calculated from literature enthalpies of formation and Third Law entropies for the species. The determination of errors through regression analysis and combination of errors is a very useful exercise for the students, allowing them to quantitatively assess the validity of their results. The students are then able to discuss the precision and accuracy of their results as well as their significance in terms of the reaction equilibrium. This is a new variation of a classic experiment that allows students to learn more about the thermodynamics of equilibrium and simple FTIR spectroscopic techniques.

Aims and Objectives

This experiment investigates the thermodynamics of a simple equilibrium process, namely the dimerisation of NO_2 to N_2O_4 and is directly integrated with the lectures where the NO_2 / N_2O_4 equilibrium is used as an example for the determination of thermodynamic parameters. It does so by measuring a portion of the infra-red spectrum as a function of temperature. The portion of the spectrum analysed allows the calculation of absorbances and hence concentration of the two species present in the mixture. This in turn enables calculation of the equilibrium constant *K* as a function of temperature. The temperature dependence of *K* allows determination of the enthalpy change for the process via the van't Hoff isochore equation. Using this value and the standard Gibb's free energy change for the reaction at 25 °C (determined from interpolation of the results for *K*), the standard entropy may be estimated.

The aims of the experiment are to enable students to understand the basic relationships governing thermodynamic quantities in a practical context, and how these quantities might be evaluated experimentally. The determination of thermodynamic quantities such as *K* or $\Delta H°$ is relevant to all science based students to deal with reactions and change. The choice of the particular equilibrium to be studied is based upon its simplicity. Despite the slightly hazardous nature of the NO_2 / N_2O_4 mixture the experiment is simple to use and is an extremely effective learning tool in that the students can visualise clearly the changing concentrations of the species and hence equilibrium constant through the changing peak absorbances as a function of temperature. Other aims of the experiments are to introduce students to modern FTIR spectroscopic techniques and equipment and help improve their analysis and manipulation of data through the use of spreadsheet/graphing software. The ideas and skills learned by students in this experiment are generically useful to a wide range of areas. It shows clearly how changes in experimental conditions disturb equilibrium and how modern spectroscopic techniques may be used to monitor this. This is relevant to all science students, be they biological chemists or atmospheric spectroscopists.

Level of Experiment

Second year undergraduate

Keyword Descriptions of the Experiment

Domain
physical chemistry

Specific Descriptors
NO2 - N2O4 equilibrium, van't Hoff equation, enthalpy change, entropy change, Gibbs free energy change

Course Context and Prerequisite Knowledge and Skills

This experiment is current taught as part of a second year Physical Chemistry subject primarily for Chemistry and Medicinal Chemistry Majors. Consequently assumed knowledge is generally 100 Level Chemistry and a basic understanding of equilibrium and heats of reaction. Two major portions of this second year subject are thermodynamics and spectroscopy. The lecture component of the course introduces students to the Laws of thermodynamics, the relationships between the fundamental thermochemical quantities needed in this experiment. The lecture course also introduces vibrational and rotational spectra of diatomic molecules. This is useful for understanding the experimental method used to study the equilibrium process. Prior knowledge of FTIR is not necessary, but the experiment acts as a useful familiarisation of the technique and gives the students a basic understanding. Basic spreadsheeting and graphing skills are not formally taught as part of the course, however, a number of the practical experiences encourage the students to use and develop their skills in this area.

Time Required to Complete

Prior to Lab: 1 h
In Laboratory: 2 - 3 h
After Laboratory: 3 h

Experiment History

The NO_2 - N_2O_4 equilibrium has long been a classic system to study. This has normally been carried out either by pressure measurement as a function of temperature. (Matthews, 1985, p. 95) or by visible spectrophotometry (Levitt, 1973, p. 189). The use of FTIR as a means of quantifying the equilibrium process is a new one. The original experiment was designed by David Griffith at University of Wollongong. The current experiment is the latest version.

References

Levitt, B. P. (Ed.). (1973). *Findlay's Practical Physical Chemistry* (9th ed.). London: Longman, p. 189.

Matthews, G. P. (1985). *Experimental Physical Chemistry.* Oxford, UK: Oxford University Press, p. 95 (experiment 3.3).