Thermodynamics of the NO2 - N2O4 Equilibrium by FTIR

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Practical:

Summary: 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 ^oC (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 DH^o 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.

Abstract

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.

Duration

Prior to Lab	1 hr
In Laboratory	2-3 hr
After Laboratory	3 hr

Further comments

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