Report DDR – Determining molar enthalpy and entropy (at normal boiling temperature) of vaporization for Acetone and n-Hexane

1. Introduction

In order to induce vaporization, the phase transition of liquid to gaseous at boiling temperature, of a substance, heat must be provided to the system. Under the condition that vapor pressure and temperature (Zeichen) remain constant during vaporization, the thermal energy provided to the system per mol of vaporized substance equals its enthalpy of vaporization (Zeichen).

For the small temperature range of the experiments detailed further on, enthalpies of vaporization can be treated as material constants. (Vgl tabellen in pdfs)

Claudius clapeyrons model, (6.4)

Where vg and vl are the molar volumes of the substance in its liquid and gaseous forms, treats vapor pressure as a function of boiling temperature T with the coexistence curve between liquid and gaseous phases for a graph, and describes the change dp expected for a variation of dT in the substance’s boiling temperature.

Taking into account that vg >> vl, and provided the gaseous phase behaves according to ideal gas law (6.5) the differential equaition can be simplified to

(6.6)

Integration yields 6.7

Where p0 and T0 are atmospheric pressure and normal boling temperature at atm. P respectively.

The substance’s entropy of vaporization at normal boiling temperature can be calculated via the Gibbs-Helmholtz equation delta G = delta vh – T , knowing that delta G = 0 for reactions that have reached an equilibrium.

A phase transitions from the liquid to the gaseous phase can also take place below boiling temperature and vapor pressure. This can be observed for example when blow-drying one’s hair or upon stepping out of the water as the droplets on the skin gradually evaporate. This is possible, because energy levels of the molecules inside the substance differ and some molecules have enough energy to overcome the threshold of the inter-molecular forces binding them to the liquid.

The molecule’s transition from fluid to gaseous phase requires energy which is taken from the fluid in the form of thermal energy, causing a momentary drop in temperature. If the fluid shares an interface with another substance (for example the skin) which has a higher temperature, it will in turn take energy from this surface to compensate for the deficit. These changes in temperature are very minor but can be measured for example if the interface is shared with a highly sensitive temperature sensor. The recorded temperature drops at contact with the sample and return to its previous value once the entire liquid has evaporated, presenting as a downward peak in a diagram where the sensor’s temperature is plotted against time. The area under the peak, established as A, which is calculated form the data obtained from the sensor, is proportional to the thermal energy taken by the liquid from the sensor during that time: 6.15

where k is a proportional factor and n is the amount of substance given in mol.

The molar enthalpy of evaporation of the substance can be calculated from this using a reference substance with a known molar enthalpy of evaporation as follows:

6.17, 6.18.

Where rho is the sample’s density, determined separately or taken from known literature.

1. Experimental
   1. Chemicals (CAS codes hinzufügen??)

The following experiments were conducted using Acetone (M=58,8g/mol), from SIGMA ALDRICH, puriss. p.a., (grössergleich) 99,5%, n-Hexane (M = 86,18g/mol), from SIGMA ALDRICH, (grössergleich) 95% and Methanol (M=32,04 g/mol), from VWR Chemicals, (grössergleich) 99,9%. All chemicals were used forgoing (any) further purification. (provided by lab hinzufügen???

* 1. Procedure

A total of 3 experiments were prepared and carried out/executed as follows:

1. The identity and purity of Acetone and n-Hexane were verified by determining their respective refractive index and density.

Refractive index measurements were done via digital refractometer (ATAGO RX-5000 (Fig.?) operating at standard wavelength of 589.0 nm (D-line) and with samples maintained at a constant 20.0 +/- 0.02°C by a LAUDA E100 circulation thermostat (attached to the refractometer). After ensuring the glass surface of the sample block was dry, a small amount of liquid was applied - just enough to cover the circular surface – and once equilibration was reached as indicated by the temperature (on the) display, measurements could be initiated.

Density was determined in two different ways.

First, by Methode A filling a 25 +/- 0.04ml volumetric flask (insert marke) with either liquid and measuring its mass using a METTLER-TOLEDO AG204 Delta Range analytical balance, the accuracy range of which is/was/ can be assumed at/to be (at) around +/- 1mg.

And secondly, by Method B, using/ with the help of an ANTON PAAR DMA 48 density gauge Fig?, where the respective sample was carefully inserted via plastic syringe and - after visual confirmation that there were no air bubbles inside the u-shaped glass tube - run at setting “F505”. Between measurements of different samples, the tube was rinsed with deionized water and dried by inducing airflow.

1. The boiling temperatures of Acetone and n-Hexane were measured at different pressure settings.

For this purpose, a two necked flask containing the sample and about 10-15 boiling stones and filled to approximately half (its) capacity was attached to a preprepared setup (fig x. explain setup), omitting grinding grease due to the risk of contaminating the sample and comparatively low significance of a tight seal in this experiment.

(Only) After ensuring that all openings were closed, the BÜCHI VAC V-503 vacuum pump, dimroth condensation cooler and WINKLER WHLG2 laboratory heating mantle with a WL10 heating controller were turned on. It is important to note that forgoing the former here and starting the cooler before sealing the system would allow water vapor from the air to condense inside the cooler and likely lead to falsified results.

While maintaining a low heat supply via the controllable heating mantle, pressure within the system was steadily decreased under close surveillance through evacuation by means of a BÜCHI I-100 vacuum controller and a ventilation valve until about 150 mbar/ 100 mbar were reached for Acetone/ n-Hexane respectively and the liquid was simultaneously boiling inside the flask and dripping steadily from the cooler. For acetone we could not observe any dripping at first, yet the liquid seemed to be boiling and the temperature was quickly decreasing to under 10°C. We concluded that the vapor currently forming would be at a lower temperature than the liquid in the dimroth cooler, causing it to escape into the separator instead of condensing. As such we increased our heat supply and not long after, equilibrium returned to the system and steady dripping could be observed.

The temperature measured by the GREISINGER GMH 3210 digital temperature gauge (with a resolution of 0.1 K) was marked down with its corresponding pressure point and the pressure was incremented in 25-50 mbar steps until reaching 900 mbar, waiting for the temperature to level out after each increase and recording respective values. This was repeated at decreasing pressure, generating two sets of values for each sample.

1. The evaporation cooling effect of Acetone, n-Hexane and Methanol (reference sample) were visualized and recorded by measuring the surface temperature of an ultra-sensitive heat sensor at 0.25s intervals during the evaporation of a predefined volume of liquid sample applied to the sensor.

The setup, a TREVAC-apparatus (transient evaporation cooling) Fig. x, self-developed by the PCL at ETH Zürich, relies on a LAUDA Ecoline 103 thermostat to keep the aluminium block with the NATIONAL LM 35 heat sensor at its center at a programmable base temperature of T0 = 35°C, deviating less than +/-0.01K.

T0 was selected at 30-40 K below the boiling point of the lowest-boiling liquid.

The sample was inserted at a steady pace via a HAMILTON 801 RN microliter syringe (scale facing forward to ensure measurement circumstances were as similar as possible for each sample inserted), using a measuring gauge to measure out exactly 5myl and discard any excess liquid beforehand.

The registered surface temperature over time was recorded via analog/digital converter (ADC, 23 bit) and broadcast on the display of a laptop attached to/that is part of the setup.

This process was carried out 3 times per substance, leaving enough time for the sensor to equilibrate back to T0 between the end of each prior evaporation and insertion of the current sample.

The R software environment [number?] (version) was used for data processing, model parameter estimation and presentation. All scripts can be found in the appendix.

1. Results and discussion

All results at a 95% vertrauensintervall?

* Compare dichte und brechungsindex to literature verify specifications (plot it in r?) dampfdruck aus kurve von experiment 1 extrapolieren? Schauen, ob mit wert übereinstimmt?
* The refractive index and density of Acetone were measured at nd=1,35867 and rho = 0.7903 g/ml (method B) respectively and the density of Acetone was calculated (method A) to be 0.7904(26) g/ml corresponding with literature values of nd= 1,3588 and rho = 0,7899 g/ml. For n-Hexane values of nd = 1,37506 and rho = 0,6594 g/ml (Method B) bzw. Rho = 0.6572(22) g/ml (Method A) were obtained compare to literature values of nd = 0,3751 and rho = 0,6603 insert figure -> vgl purity given by supplier?? Lower for n-Hexane, spiegelt sich in den results wieder.

1. References

* NIST
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1. Appendix
2. Acknowledgements