A 3 Vapor pressure of volatile liquids

Purpose

The purpose of this experiment is to determine the vaporization enthalpy, entropy and the boiling point at normal pressure for several intentionally chosen volatile liquids. These quantities can be derived from the vapor pressure curve **p**(T) which has to be recorded during heating the liquid.

Hazard evaluation

Some hints:

The possible hazard originating from the sources listed below should be considered and estimated:

1. Chemicals used in the experiment (one should evaluate the hazard and risks associate with handling of volatile liquids, ethanol acetone, methanol).
2. Technical instruments (in particular handling of glass accessories).
3. Handling of the very hot and very cold substances and accessories.

Theoretical Backgrounds

For a multicomponent and multiphase system in equilibrium the general Gibbs's phase rule applies:

$$P + F - K - 2 = 0 \tag{1}$$

where, P: die number of different phases in the system

F: the number of freedom degrees

K: the number of different components in the system

Example: When considering two different phases of a pure substance in equilibrium then K=1 und P=2, i.e there is exactly one degree of freedom, F=1. Consequently the p-T diagram is constituted by exactly one curve p=f(T). Depending on the phases involved (e.g. different temperature regions of the same substance) the resulting p(T) curve mirrors the melting, the sublimation or the vaporization curve. All three cases can be described by the Clapeyron equation:

$$dp / dT = \Delta S / \Delta V = \Delta H / T \Delta V \tag{2}$$

ΔS, ΔV and ΔH represent the differences in the molar entropy, enthalpy and volumes for both phases.

In the case of a vapor curve of a pure liquid the volume of the liquid is very small in comparison to the vapor and can be entirely neglected. Consequently for quantification of the system one can apply the state equation for ideal gas and combine it with eq. (2):

$$d \ln p / d(1/T) = -\Delta H_V / R \qquad (3)$$

and after integrating the equation over a limited space ($p_1 - p_2$) and ($T_1 - T_2$):

$$ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta H_V}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (4)$$

ΔH_V is the vaporization enthalpy, R is the gas constant.

For the case of the normal pressure, (p=1013 hPa) is the boiling temperature of the liquid T_1 and the term $\Delta H_V/T_1$ represents the corresponding entropy ΔS_V. By plotting the function $\ln(p_2/p_1)$ versus 1/T one gets a straight line with a negative slope $-\Delta H_V/R$ and a intercept of $\Delta S_V/R$. This property constitutes the method for determination the required quantities: ΔH_V and ΔS_V.

Realization of the experiment

1. Strategy of the Measurement

The experiment starts with the fabrication of a clean liquid/vapor-system (two phases in equilibrium): A volatile liquid with its vapor both deposited in a closed bulb, (constant volume). First, the system has to be cooled down to a temperature T* (-14÷-16 °C) by contacting the filled glass bulb with an ice-water chiller. The real measurement can be started when the lowest temperature T* stagnates and the warming of the system sets on. (The slow warming results from the heat exchange between the ambient air and the liquid in the ice-water chiller). The detection of the vapor-pressure curve, p(T), proceeds via a synchronous read out of the (p,T) data pairs as a function of progressing system warming (environmental heating). The system studied here is stored in an isolated glass bulb which is equipped by sensitive pressure and temperature sensors.

2. Leak test

First, the vacuum apparatus has to be tested for leak tightness, i.e. the final vacuum (saturation pressure) reached after evacuating the whole system without the liquid should reach a level better than 0.1 mbar and stay at this level after closing the valve (without pumping).

3. Fabrication of a clean liquid/vapor system

The glass bulb can be removed from the vacuum apparatus first after venting the whole system. Subsequently the glass bulb has to be filled by the chosen liquid up to ~1/3 of its inner volume. The filled glass bulb has to be connected with the pumping system again via the grease lubricated glass connector and subsequently the whole system has to be evacuated by using a rotary pump. As soon as the rotary pump reached the best vacuum (saturating vapor pressure) the connecting valve will be closed and the glass vessel should be slightly warmed up (by heat from your hand touching the bulb for a while) to evaporate a small amount of the substance and consequently remove the residual air from the glass bulb. The newly created vapor (still contaminated by residual air) has to be removed by opening the valve again and pumping away the vapor in the glass bulb. This cycle has to be repeated three times.

4. Cooling down the system

The filled and evacuated glass bulb is now prepared for the next step. First, it has to be cooled down to T*(~-15 °C) by diving it partly into an ice-water chiller (under a slow but permanent stir the ice/water mixture by hand). Unfortunately, in our setup the current temperature of the system studied here can be measured only by touching the finger of the digital thermometer to the outer side of the filled glass bulb (only reduced precision achievable). In order to improve the thermometer/liquid contact some glycerin droplets have to be added. Thus, this set up requires longer times for reaching thermodynamic equilibrium between the inner and outer sides of the system. The cooling stage becomes completed when the lowest temperature of the system T* levels off at ~-15÷-16°C and keeps constant for longer time. Now the spontaneous warming of the system can set on (the temperature of the cooling medium starts to increase due to the heat exchange with the ambient air)

5. The measurement of the vapor-pressure curve, p(T)

The spontaneous warming of the whole system manifests itself by slow increase of the temperature T which results in further increase of the vapor pressure, p. The temperature increase in the liquid/vapor-system can be slightly accelerated by admixing small amount of tap water to the ice-water chiller (under permanent slow stir the ice/water mix). Now the p(T) curve can be determined by periodic (t_n= 120 n [s], n=0,1,2..) reading out the (***p***(t_n),***T***(t_n)) data pairs averaged over a time interval of ~25 seconds. It is sufficient to get one averaged data pair with a constant time interval of 2 minutes (t_n=120 n [s], t_0=0 when T* starts to increase). One has to read out a sequence of 5 data pairs (p_i,T_i) with a time interval of 5 second each. Subsequently the related mean values (***p,T***) have to be calculated per definition: ***p***=(p_1+p_2+p_3+p_4+p_5)/5, ***T***=(T_1+T_2+T_3+T_4+T_5)/5). All measurements have to be performed under permanent and slow stir the ice/water mix in the chiller). The monitoring of the (p,T)-evolution can be stopped when the liquid temperature reached the room temperature (~20 °C). The data pairs yielded in this experiment should be plotted as ln(p_2/p_1) versus 1/T. According to the Clapeyron equation one expects to obtain a straight line which enables to derive the vaporization enthalpy ΔH_V from the slope and the vaporization entropy ΔS_V from the intercept.

Data processing

1. One has to plot the **p**(**T**) function and determine the slope of the tangential straights for several representative points (covering the full data range): ΔH_V.
2. As the second method, the function ln(p_2/p_1) has to be plotted versus 1/T and subsequently the quantities ΔH_V und ΔS_V have to be derived from the plot.
3. From the plot the value of the boiling point for the substance investigated should be given (at normal pressure of 1013 hPa)
4. By means of the Trouton’s rule the normal boiling point should be calculated and compared to the value determined here.
5. The Clapeyron’s equation should be derived from the main theorems of the thermodynamics.

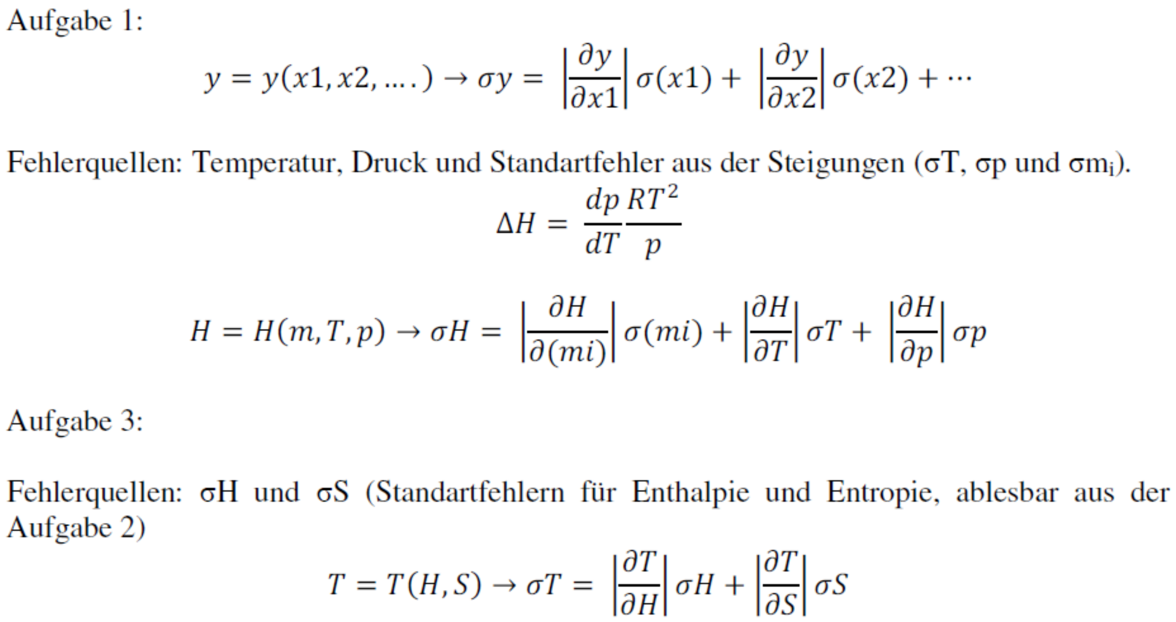
Selected topics you have to know before starting the experimental work:

Phase diagram of pure substances, Gibbs's phase rules, Thermodynamic conditions for an equilibrium, Clausius–Clapeyron equation; evolution of the thermodynamic function under phase transitions (all as functions of temperature); several examples for application of the Trouton's rules.

Further Questions

1. Assuming that the vapor of the investigated liquid contains an additional inert gas (e.g. ingredients, impurities) which does not solvate in the host vapor. How the vapor pressure curve p(T) becomes influenced by inert gas?
2. How the curvature of the liquid surface modifies the vapor pressure? (droplets vs flat surface)

Estimation of experimental errors



Aufgabe 1:

$$y = y(x1, x2, \dots.) \rightarrow \sigma y = \left|\frac{\partial y}{\partial x1}\right| \sigma(x1) + \left|\frac{\partial y}{\partial x2}\right| \sigma(x2) + \cdots$$

Fehlerquellen: Temperatur, Druck und Standartfehler aus der Steigungen (σT, σp und σm_i).

$$\Delta H = \frac{dp}{dT}\frac{RT^2}{p}$$

$$H = H(m, T, p) \rightarrow \sigma H = \left|\frac{\partial H}{\partial (mi)}\right| \sigma(mi) + \left|\frac{\partial H}{\partial T}\right| \sigma T + \left|\frac{\partial H}{\partial p}\right| \sigma p$$

Aufgabe 3:

Fehlerquellen: σH und σS (Standartfehlern für Enthalpie und Entropie, ablesbar aus der Aufgabe 2)

$$T = T(H, S) \rightarrow \sigma T = \left|\frac{\partial T}{\partial H}\right| \sigma H + \left|\frac{\partial T}{\partial S}\right| \sigma S$$

Experimental Setup