

## VAPOR PRESSURE AND HEAT OF VAPORIZATION

### A) Theoretical

We study the liquid-vapor phase equilibrium of a one-component system in this measurement. Such a system is of one degree of freedom as the phase rule of Gibbs points out:

$$F = C - P + 2 = 1 - 2 + 2 = 1 \quad 1)$$

One of the intensities (potentials) is independent and the equilibrium values of the others are determined by it. Setting the temperature determines the equilibrium vapor pressure and setting the pressure determines the equilibrium temperature. The relative quantities of the two equilibrated phases can not be determined by any way of setting intensities, it depends on extensities as total number of moles and volume.

The two phases, liquid and vapor, are in equilibrium if the rate of vaporization and that of condensation are compensated by each other:

$$i_{\text{vaporization}} + i_{\text{condensation}} = 0 \quad 2)$$

and consequently, the quantity of both phases remains unchanged. Since both vaporization and condensation are driven by some potential, condition 2) induces an other condition: these potentials must have the same value. The equilibrated potentials must be chemical potentials in this case as we are dealing with molar fluxes and the amount of material possesses chemical potential as conjugated intensity:

$$\mu_{\text{liquid}} = \mu_{\text{vapor}} \quad 3)$$

Chemical potentials must be unchanged in equilibrium, so Eq. 3) holds true of differential form, too:

$$d\mu_{\text{liquid}} = d\mu_{\text{vapor}} = 0 \quad 4)$$

Since we are given one-component phases, chemical potentials in Eq's 3) and 4) can be replaced by molar Gibbs free energies (isotherm-isobar ones, of course):

$$G_{m,\text{liquid}} = G_{m,\text{vapor}} \quad 5)$$

and

$$dG_{m,\text{liquid}} = dG_{m,\text{vapor}} \quad 6)$$

,respectively.

Substitution of the expression of the differential of Gibbs free energy in Eq. 6):

$$V_{m,\text{liquid}} dp - S_{m,\text{liquid}} dT = V_{m,\text{vapor}} dp - S_{m,\text{vapor}} dT \quad 7)$$

yields the Clapeyron equation:

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T \cdot \Delta V_m} \quad 8)$$

Here we have taken into account that  $dH=T \cdot dS$  under isobar condition and, as our condition is isotherm as well, its integral is  $\Delta H=T \cdot \Delta S$ .

Of course, the Clapeyron equation holds true of the phase equilibrium of any other one-component two-phase system, not just liquid-vapor.

Vaporization is considered to be positive in the differences of Eq. 8):

$$\Delta S_m = S_{m,vapor} - S_{m,liquid} \quad 9)$$

$$\Delta V_m = V_{m,vapor} - V_{m,liquid} \quad 10)$$

$$\Delta H_m = H_{m,vapor} - H_{m,liquid} \quad 11)$$

Heat of vaporization is the enthalpy difference in Eq. 11).

Integration of the Clapeyron equation may become a difficult task as, in the most general case, both heat of vaporization and change of molar volumes depend on temperature and pressure. The problem may be simplified by assuming that molar volume of the liquid can be neglected and the vapor obeys the perfect gas law:

$$\Delta V_m \approx V_{m,g\ddot{o}z} \approx \frac{RT}{p} \quad 12)$$

Substituting this expression to Eq. 8) and assuming the heat of vaporization to be constant one gets a readily integralable differential equation:

$$\frac{dp}{p} = \frac{\Delta H_m}{R} \cdot \frac{dT}{T^2} \quad 13)$$

whose integral yields the original form of the Clausius-Clapeyron equation:

$$\ln p = -\frac{\Delta H_m}{R} \cdot \frac{1}{T} + C \quad 14)$$

(C is the integration constant.)

A better agreement with experimental results can be achieved while mantaining the simple form if one modifies the perfect gas law by use compressibility factors to calculate the molar volumes of vapor and liquid:

$$\Delta V_m = \frac{RT}{p} \cdot (Z_{vapor} - Z_{liquid}) = \frac{RT}{p} \cdot \Delta Z \quad 15)$$

Replacing change of molar volumes from Eq. 15) to Eq. 8) and assuming that  $\Delta H_m / \Delta Z$  is independent of temperature one gets the ordinarily used form of the Clausius-Clapeyron equation:

$$\ln p = -\frac{\lambda}{R} \cdot \frac{1}{T} + C \quad (16)$$

$$\text{,where } \lambda = \frac{\Delta H_m}{\Delta Z} \quad (17)$$

$\lambda$  defined in Eq. 17) is the apparent heat of vaporization.

The heat of vaporization may not be independent of temperature since it must become zero at the critical temperature, consequently, it must be its decreasing function.  $\Delta S_m$ , and  $\Delta V_m$  and, by virtue of the latter,  $\Delta Z$  have the same tendency. It is quite reasonable to expect a considerably milder temperature dependence for virtual heat of vaporization than for heat of vaporization. Experience supports this expectation.

According to Eq. 16)  $\ln p$  is a linear function of  $1/T$ . The apparent heat of vaporization can be given by multiplying the slope of this plot with  $-R$ .

## B) Equipment

We use a U-shaped manometer filled with mercury to measure the vapor pressure. (See the attached figure.)

It consists of a closed vessel 1 and an open one 3 connected to each other by a flexible tube 2. Column of mercury keeps liquid and vapor closed in vessel 1 and it meets atmospheric pressure in the open vessel 3. A larger vessel 4 may be filled with water of different temperature to thermostate the content of vessel 1. The open vessel is attached to the end of a tape measure 5 with whose aid one can change its position. The position of the open vessel can be fixed with a locking 6.

Since the level of mercury can be read only in the right side of the manometer the level in the left side must be fixed. The O-ring 8 on the closed vessel serves this goal. Before reading the manometer one has to lift or sink the open vessel until mercury-level in the closed vessel meets the O-ring. As the bridle 7 of the locking should have identical position with the O-ring one has to read the levels at the bridle ( $h_1$ ) and at the mercury surface in the open vessel ( $h_2$ ) on the tape measure. In order to know the atmospheric pressure ( $b$ ) there is a mercury barometer in the laboratory. In an ideal case, the vapor pressure, in mm's of mercury (Hgmm) is

$$p_{\text{vaporz}} = b - (h_1 - h_2) \quad (18)$$

In reality some corrections are to be made on Eq. 18).

A) *Bridle correction*: With the aid of a builder's level (or at least a ruler) we must check if the levels of O-ring and bridle are the same. If not, the difference must be added to (or subtracted from)  $h_1$ .

B) *Hydrostatic pressure correction*: The vapor pressure in Eq. 18) contains the hydrostatic pressure of the liquid, too, which should be subtracted from it. The height of the liquid-column (usually 2-3cm) can be measured with a ruler, the density of the liquid can be gained from tables of handbooks. Since density of mercury exceeds that of an organic liquid at least by an order of magnitude, this correction is 1-2 Hgmm. Its negligence causes an error less than 1% in most cases (however this error is systematic).

C) *Temperature correction*: Density of mercury decreases as temperature increases, consequently, a given  $h_1-h_2$  means less pressure-difference at higher temperature than at lower one. There is a table at the barometer containing additive

correction factors  $a$  as function of temperature and pressure. This correction can be practically connected to conversion of unit of pressure to Pa.:

$$p_{\text{vapor}} / Pa = p_{\text{vapor}} / Hgmm \cdot \frac{101325 Pa}{760Hgmm} \cdot \frac{760Hgmm + a}{760Hgmm} \quad 19)$$

D) *Air correction*: Despite of all care, some amount of air may be present in the closed vessel. It causes the measured vapor pressure to be dependent on the vapor/liquid-volume ratio: the larger the latter is the smaller it is. In order to determine the volume of vapor phase some assumptions are needed:

- a) air does not dissolve in the liquid;
- b) the volume of the liquid is constant;
- c) both air and vapor obey the perfect gas law;
- d) by lifting of the open vessel one can compress air in the closed vessel to a bubble whose volume is negligible comparing with volume of the vapor phase during measurements.

As the volume of the flexible tube is constant, changes in the mercury-volumes in the closed and that in the open vessel, apart from opposite signs, must be equal if the conditions above are fulfilled. The pressure measurable under Eq. 18) is the sum of the vapor pressure and the partial pressure of air. It writes for measurements 1 and 2 carried out on the same temperature:

$$p_1 = p_{\text{vapor}} + p_{\text{air},1} = b - (h_{1,\text{corr},1} - h_{2,1})_{\text{corr}} \quad 20a)$$

$$p_2 = p_{\text{vapor}} + p_{\text{air},2} = b - (h_{1,\text{corr},2} - h_{2,2})_{\text{corr}} \quad 20b)$$

(Subscript "corr" designates bridge correction at  $h_1$  and conversion/correction according to Eq. 19) at the right bracket.)

Subtracting Eq. 20a) from Eq. 20b):

$$p_2 - p_1 = p_{\text{air},2} - p_{\text{air},1} = (h_{1,\text{corr},1} - h_{2,1}) - (h_{1,\text{corr},2} - h_{2,2})_{\text{corr}} \quad 21)$$

and by virtue of condition c):

$$p_{\text{air},2} = p_{\text{air},1} \cdot \frac{V_1}{V_2} = p_{\text{air},1} \cdot \frac{h_{2,1} - h_{2,3}}{h_{2,2} - h_{2,3}} \quad 22)$$

where  $h_{2,3}$  is the mercury-level in the open vessel when air is compressed to its minimum volume.

After substitution of the partial pressure of air in measurement 2 ( $p_{\text{air},2}$ ) to Eq. 21) from Eq. 22) one can express its value in measurement 1:

$$p_{\text{air},1} = (p_2 - p_1) \cdot \frac{h_{2,2} - h_{2,3}}{h_{2,1} - h_{2,2}} \quad 23)$$

This is the value of air correction we have to subtract from the pressure calculated with Eq. 19), assuming that the level of mercury was at the O-ring during measurement 1. It is to be converted for other temperatures with the perfect gas law.

### C) Experimental

1. Measure bridge correction
2. Read the barometer and its thermometer. Decide the correction factor from the table.
3. Determine the air correction by measuring the levels  $h_1$  and  $h_2$  when the mercury-level in the closed vessel is
  - at the O-ring (measurement 1);
  - between the O-ring and the maximum (measurement 2);
  - at its maximum (air compressed to its minimum, measurement 3).

Do not forget to measure the level-difference of the O-ring and the mercury-surface when measuring  $h_{1,2}$ . One can use a ruler to do that. Measuring  $h_{1,corr,3}$  is not needed.

4. Lift up the open vessel to its maximum position and fill up vessel 4 with water whose temperature almost reaches the atmospheric boiling point of the measured liquid. After 1-2 minutes and some mixing the equilibrium has been settled. Read  $h_1$ ,  $h_2$  and the thermometer of vessel 4. Set a new temperature by making use of natural cooling or adding cooler (or warmer) water to vessel 4.

5. Calculate the vapor pressure for each temperature using Eq.18) and 19).

6. Calculate the air correction for room temperature by using Eq.21) and 23). Convert its value for other temperatures with the perfect gas law. Subtract the air corrections from the vapor pressures calculated under 5.

7. Draw two plots:

$$p_{\text{vapor}} / \text{Pa} - T / ^\circ\text{C}$$

and

$$\ln p_{\text{vapor}} - T^{-1} / \text{K}^{-1}$$

Read the slope of the latter and calculate the apparent heat of vaporization.

