KEMS448 Physical Chemistry Advanced Laboratory Work

The Determination of Absolute Zero

1 Theory

According to the general equation of state for ideal gases,

$$pV = nRT = Nk_BT, \tag{1}$$

in a constant pressure system containing a constant amount of ideal gas, the volume of the gas is linearly proportional to its temperature. In the molecular, statistical interpretation, raising the temperature increases the mean velocity of the gas molecules, and the rate with which they collide with the container walls increases, increasing the volume the gas takes up. By measuring gas volumes at different temperatures, the temperature can be extrapolated to where the volume is zero, meaning the gas has no kinetic energy left. This temperature is the same for all gases, the absolute zero temperature ($0\ K = -273{,}15\ ^oC$). In practice, when decreasing the volume in a constant pressure, real gases tend to liquify before the absolute zero can be reached.

Regular air indoors is a mixture of gases (N_2, O_2, Ar, CO_2, H_2O etc.). According to Dalton's law, the total pressure of an ideal mixture of gases is the sum of partial pressures from each of the ideal gas in the mixture.

$$p = p_A + p_B + ... = \sum_J p_J, \tag{2}$$

where

$$p_J = \frac{n_J RT}{V}. \tag{3}$$

Based on Dalton's law, the partial pressure of dry indoor air p_{air} can be determined in a certain temperature by subtracting the vapour pressure of water p_{H_2O} from the external air pressure p_e

$$p_{air} = p_e - p_{H_2O}, \tag{4}$$

which gives for the water vapour volume

$$V_{H_2O} = V\frac{p_{H_2O}}{p_e}, \tag{5}$$

where V is the total volume of the gas mixture. The partial volume of the dry indoor air can be derived through the total volume of the gas mixture and the partial volume of the water vapour

$$V_{air} = V - V_{H_2O} = \frac{V}{p_e}(p_e - p_{H_2O}) = V\frac{p_{air}}{p_e} \tag{6}$$

It is crucial to use the volume of dry indoor air in determining the absolute zero, since the vapuor pressure of water is not linearly dependent on temperature, which would cause curvature in high temperatures on the graph where the volume is plotted against temperature.

2 Experimental methods

Fill a slim beaker of 1 l up to about 90 % of its volume with water. Put about 10 ml's of water into a graduated glass cylinder, up to about 80 % of its total volume (not 8 ml, though), use a finger as a cork and place the cylinder upside down into the beaker (see figure 1). Make two of these for parallel measurements.

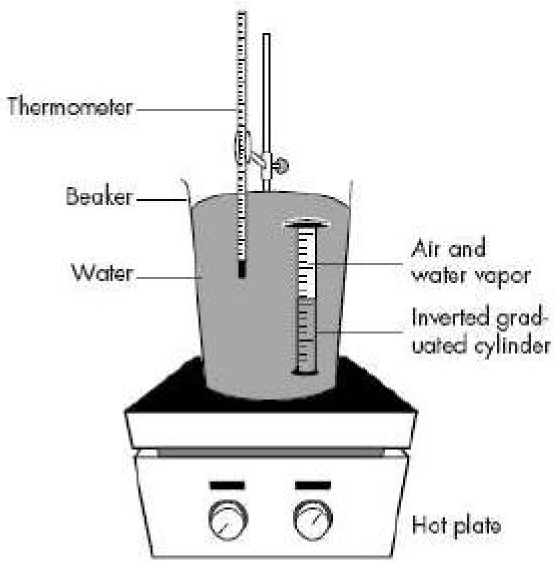

Figure 1: *The measuring equipment for determining the absolute zero.*

The cylinder should be completele submerged into the water, so add water into the beaker, if necessary. Lift the beaker onto a heating plate and put a thermometer into the beaker. Heat the water up to about 80 ^oC temperature and lift the beaker off the heating plate onto the fume chamber table (use rubber gloves with padding in them). Read the first air volume from the glass cylinder, taking an even value from one particular line in the temperature range $70 - 80$ ^oC and continue down from there as the system cools down, taking volume values about every 5 ^oC, until about zero celsius. Reaching the zero might not be possible, but about 2 degrees is acceptable. Use ice cooling atrting from a point that you see fit (at about 40 ^oC is reasonable). Place the ice gradually, small amounts at a time, into the beaker and wait for the system to stabilize.

Straighten the glass cylinder every time you write down a value and always read the scale from the same eye level. In temperatures higher than 50 ^oC, distracting air bubbles may form onto the container's outer walls. These can be removed by rubbing the surface with a glass rod. Let the system find a new thermodynamic equilibrium at each measurement temperature before writing down the values, this should take a few minutes.

Making the second parallel measurement can be done by putting the second beaker onto the hot plate right after you take the first one off of it. Two different systems enable you to take a mean of the value for every temperature measured, for the corresponding volumes.

Finally, read the indoor air pressure from the mercury barometer inside the laboratory.

3 Analyzing the results

Find the values of the water vapour pressure curve from a book of tables like the CRC *Handbook of Chemistry and Physics*. Use values as accurate as possible, so if the exact temperature you want is not on the tables, interpolate from the curve. Calculate and tabulate the dry indoor air volumes with the help of equations 4 through 6. Plot temperature against dry indoor air volume and from the linear fit, extrapolate the value for the absolute zero temperature, and estimate the molar amount of dry air in the glass cylinder. Estimate the error values from the linear fit. Additionally, compare the two different measurements and their errors, and consider and comment on the possible errors in the whole laboratory work.

The absolute zero temperature cannot be achieved experimentally, but in certain cases, people have achieved values quite near it. Briefly discuss how these "world records" have been achieved. Are there negative values on the Kelvin scale? Justify your answers.

References

[1] Atkins P.W., de Paula J., *Physical Chemistry*, 8th Edition, Oxford University Press

[2] Kim M., Song Kim M., Ly, S *A Simple Laboratory Experiment for the Determination of Absolute Zero*, J. Chem. Ed., **2001**, 78, Vol. 2.