## VAPOUR PRESSURE OF WATER

## REFERENCES

G.R. Noakes. New Intermediate Physics. Copies are available at the Resource Centre.

## THE EXPERIMENT



The purpose of this experiment is to study the variation of the vapour pressure of water between about 300 K and 373 K . The apparatus is shown schematically in the figure. The bulb in which the water vapour is contained has been evacuated of all gases and then filled with mercury and pure water. The pressure of the water vapour causes the mercury to rise up in the tube. (The height $h$ of the column of mercury is a convenient unit for the vapour pressure, though, of course, it needs some units conversion to be expressed in SI units.) The bulb is immersed in a water bath whose temperature can be varied and measured.

The procedure is simply to measure the height $h$ as a function of the temperature $T$ of the water in the bulb. This temperature can be quite different from the temperature of the water bath unless a) they are in good thermal contact, and $b$ ) sufficient time is allowed for the system to reach thermal equilibrium. Therefore it is very important that the water in the water bath completely covers the bulb, and that thermal equilibrium has been reached before $h$ and $T$ are measured. How can you tell when thermal equilibrium has been reached?

The measurement of $h$ requires some thought. There is a scale against which the top of the mercury column can be measured. However, the scale does not extend down to the level of the mercury in the bulb. In addition this lower point of the mercury column is not fixed, but will change slightly as the height $h$ changes. Study the apparatus and be sure you know how to measure $h$ correctly and as precisely as possible. Then check with your demonstrator that your method is the best available.

The analysis of the data of vapour pressure as a function of temperature is not based on any exact theory. But a reasonable approximation is provided by integrating the Clapeyron equation:

$$
\frac{d p}{d T}=\frac{\ell}{T\left(V_{v}-V_{\ell}\right)}
$$

where $T$ is the temperature in Kelvin, $d p$ is a small change in the vapour pressure due to a temperature change $d T$ (i.e., the slope of
 the vapour pressure - temperature curve), $V_{v}$ is the volume per mole of the vapour phase, $v_{\ell}$ is the volume per mole of the liquid phase, so that $\left(V_{v}-V_{\ell}\right)$ is the change in the volume per mole when water evaporates into a vapour, and $\ell$ is the latent heat per mole (also called the Enthalpy or Heat of Vapourisation) in the transition from a liquid phase to a vapour phase, i.e., the heat per mole absorbed in that transition.

By making two reasonable approximations,
(i) $\left(V_{v}-V_{\ell}\right) \simeq V_{v}$ the volume per mole of the vapour; and (ii) $p V_{v}=p V / n=R T$ (ideal gas law)

$$
\text { we obtain } \quad \frac{d p}{d T}=\frac{\ell}{\frac{R T^{2}}{p}} \text { or } \frac{d p}{p}=\frac{\ell}{R T^{2}} d T
$$

If we now make the important approximation that $\ell$ is independent of temperature, this equation can be integrated immediately to give:

$$
p=p_{o} \exp \left(\frac{-\ell}{R T}\right)
$$

where $p_{0}$ is a constant of integration and R is the gas constant. This equation should be valid in the temperature range this experiment is performed. Thus a plot of $\ln (p) v e r s u s 1 / T$ will be a straight line, the slope of which will give a value for $\ell$. Remember that $T$ should be in Kelvin! You should compare your value with that given in the Handbook of Chemistry and Physics.

In determining the error in your value of $\ell$, it is important to consider the possible systematic errors this experiment contains. For example:

- Is it necessary to correct for the pressure due to the liquid water in the bulb which rests on top of the mercury surface in the bulb?
- Is the water vapour at the same temperature as the water bath? Or does the mercury column conduct heat from the bulb at a significant rate?
- Should the values of $h$ be corrected for the thermal expansion of the mercury and glass*?
* The coefficient of volume expansion of mercury, $\alpha \approx 0.181 \times 10^{-3} \mathrm{deg}^{-1}$ The coefficient of volume expansion of glass, $\beta \approx 8.5 \times 10^{-6} \mathrm{deg}^{-1}$.
- Does the vapour pressure of mercury produce a significant error?

As in any other experiment, an effort should be made to estimate these errors quantitatively in order to decide whether any of them are significant.
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## Preparatory Questions.

Note: We hope that the following questions will guide you in your preparation for the experiment you are about to perform. They are not meant to be particularly testing, nor do they contain any "tricks". Once you have answered them, you should be in a good position to embark on the experiment.

1. Write down the equation for the pressure, P , at a point X , situated a distance of h below the surface of a liquid of density $\rho$ if the surface of the liquid is at zero pressure. Hint for those who haven't seen this before: the pressure is a force per unit area. Calculate the force that a column of height h and cross sectional area A would exert at point $X$ due to its weight; then divide by A to get the pressure.
2. What might be the effect on your experimental results if the water in the water bath does not completely cover the water and vapour mixture in the bulb?
3. As the pressure increases, the mercury will rise up the tube and the level of the reservoir will drop. How will you ensure that you measure the correct value of $h$, the height between the meniscus of the mercury in the tube and the top of the reservoir?
4. For the experimental results to make sense, the temperature of the water and its vapour, the mercury and the water bath must be all the same when a measurement is taken. Suggest a procedure that will ensure that this is actually the case.
5. If the experimental error in the temperature, $\mathbf{T}$, is $\mathbf{\Delta T}$, what it the error in $\mathbf{1 / T}$ ? If the error in your value of pressure is $\Delta \boldsymbol{p}$, what is the value of the error in $\ln (\boldsymbol{p})$ ?
