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NEW SYSTEM FOR TEMPERATURE DEPENDENT MEASUREMENTS OF VAPOR PRESSURES OF SUBSTANCES IN THE RANGE BELOW 1 PASCAL

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INTRODUCTION

From the field of vapor pressure measurements here specially the range of low pressures between 10^{-5}Pa and 1 Pa (1 Pa = 1 Newton/m^2) in the temperature range between 150 and 700 K shall be regarded.

A measuring method and the corresponding instrument, the vapor pressure balance suited for this range is introduced and briefly compared with another measuring method, the gas saturation method which is applied in the same pressure range.

Vapor pressure directions with the vapor pressure balance are recommended in the OECD guideline as standard method.

Important for the determination of vapor pressure $\leq$ 1 Pa.

The determination of smallest pressures in the above mentioned range within recent years became increasingly important for structural research in the field of organic chemistry, for the clarification of destillation questions and for high vacuum physics and techniques.

The environmental relevance of vapor pressure measurements is accounted for by the following reasons:

- The vapor pressure gives an indication of the probability of the phase transitions liquid/gas and solid/gas.
- The vapor pressure, together with the solubility in water, is the major auxiliary variable for calculating the volatility of a substance from an aqueous solution.
- Vapor pressure is therefore a significant factor for predicting atmospheric concentrations.
- The vapor pressure of a substance can furthermore be useful as a basis for deciding whether or not a photochemically induced degradation (in the homogeneous gas phase or in an adsorbed phase) is necessary.

Technical design and function principle of the vapor pressure balance

The arrangement consists of a highly sensitive compensation microbalance which has a sensitivity of 5.10^{-8} g with an accuracy of 10^{-7} g.

One of the balance pans is replaced by a thin gold-plated baffle plate of alumina which is ground to avoid electrostatic interferences. Below this

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baffle plate is a cylindrical evaporation cell with a capacity of 10 cm^3 which can be cooled by a cold finger as well as heated electrically by a heating coil. The evaporation cell is equipped with an opening that can be closed.

Between evaporation cell and baffle plate there is a system of interchangeable orifices. The geometry of the total assembly is chosen in such way that under high vacuum conditions a molecular beam is formed which strikes the baffle plate vertically from below and is collected there in its total cosinal distribution.

For high-vacuum generation the described arrangement is accommodated in an evacuatable recipient which must be evacuated before the measurement to 1 ... 2.10^{-3}Pa by a turbo pump or a suitable diffusion pump.

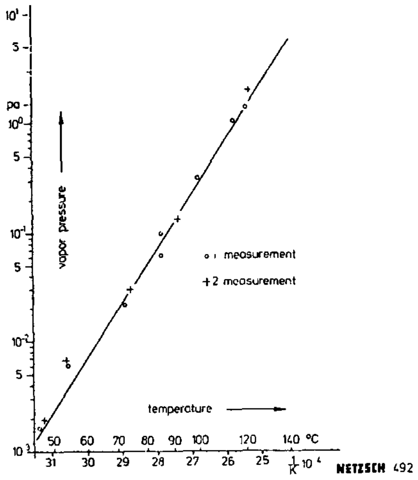
The residual gas pressure is determined by two requirements:

1. The free outlet of the residual gas molecules has to be large compared to the dimension of the molecular beam so that there will be no dispersion of the vapor molecules in the residual gas.
2. The residual gas pressure has to be smaller than the smallest vapor pressure that can be determined with the balance from the impulse of the molecular beam. Then interferences of the balance by molecular pressures of the residual gas are excluded.

Both requirements are fulfilled for the above mentioned residual pressure, as could be confirmed in experiments.

RESULTS AND DISCUSSION

Two examples of application:



Vapor pressure of
Dementon - S - methyl - sulfon

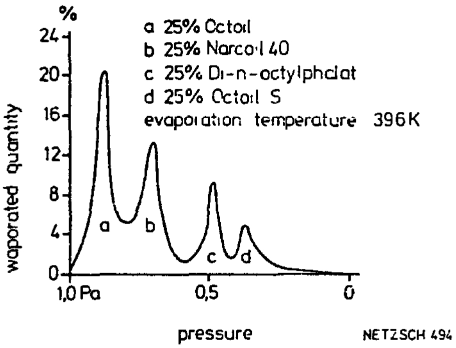
This figure shows the evaporation curve of Demeton - S - methyl - sulfon, E 158, an insecticide of Messrs. BAYER, Leverkusen. The curve points were recorded in two test runs. A very good reproducibility of the results obtained demonstrates the high quality of the instrument. Should the first curve show a higher vapor pressure, the measurement would have to be made a third time. Curves two and three would then coincide. This would mean that the substance contains easily volatile pollutions. If the curve of the third measurement deviates from the first one upwards or downwards, the tested substance has chemically reacted. The measurements then would have to be repeated at a lower temperature range.

Evaporation Analysis

To determine vapor pressure curves of substances which are composed of a mixture, i.e. of no chemical uniformity, is difficult because the composition of the sample can change in the furnace during a measuring cycle. The effect of such a change in the composition would be that the vapor pressure of the substance becomes smaller. On the other hand, following the decrease of vapor pressure you can get, within the course of time, a survey about the composition of the substance - this would be described as evaporation analysis.

When carrying through the evaporation analysis, the vapor pressure is measured at certain time intervals at constant temperature, until the sample has completely evaporated. Further from the measurement of the evaporation speed the quantity evaporated between two measuring points can be calculated, a relation between vapor pressure and evaporated quantity results.

If from such an evaporation curve those quantities are taken which have evaporated in a certain pressure range (in the following example 0,025 Pa) and if they are plotted against each average pressure, there will be an evaporation analysis as it is shown in the figure below (in principle this shows a graphical differentiation). The four maxima show that with this method individual components of a mixture can also be separated if the vapor pressures differ only slightly.



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Evaporation analysis of a mixture of each 25% a: Octoil; b· Narcoil 40; c: Di-n-octylphalat; d: Octoil S evaporation temperature 396 K

CONCLUSION

As a result of this paper we can say that measurement with a modern vapor pressure balance in the pressure range ≤ 1 Pa is an easy, quick and versatile method to determine vapor pressures. The combination of this measuring principle with automatic data processing gives the expert and scientist an instrument that delivers quickly and reliably the substance date he is searching for. There are only few cases where preference should be given to the gas saturation method. However, this does not restrict the value of this instrument.

REFERENCES

1 A. Herlet and G. Reich, Zeitschrift fur angewandte Physik, Vol. 9, 14-23 (1957)
2 personal information of Messrs. BAYER AG, Leverkusen
3 OECD Guideline 104 - Final report of the OECD Chemicals Testing Program
4 G. Kortum, Einfuhrung in die Chemische Thermodynamik, Gottingen 1966.