

solution became dark-red, 0.35 ml of hydrazine hydrate was added with cooling. After 5 min the solution was neutralized with sodium bicarbonate solution and extracted with ether. Evaporation of the dried ether solution yielded 95 mg of crude 3-(2'-furyl)pyrazole, having the same IR-spectrum as an authentic sample.<sup>5</sup> NMR-spectra were obtained with a Varian A-60 high resolution spectrometer and the mass spectra with an LKB 9000 mass spectrometer.

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## The Probe Method for Measurement of Equilibrium Vapour Pressures

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An elegant way for determination of relative vapour pressures is the "dew-point" method applied among others by Hargreaves<sup>1</sup> to copper-zinc alloys and by Birchenall and Cheng<sup>2</sup> to silver-cadmium alloys. In this method a furnace with two independently heated zones is employed. The alloy sample to be investigated is placed in one end of an evacuated silica tube. This tube is placed in the furnace in such a way that the sample is kept at a constant temperature, while the temperature of the other end of the tube is lowered until pure droplets of the volatile component just start to condense. This temperature, the "dew-point", is accurately determined by repeated heating and cooling of this coolest zone of the furnace. The vapour pressure of the pure volatile component has of course to be known as a function of temperature. The crucial point of the method is the accurate determination of the dew-point which often is difficult and besides imposes the restriction that the sample container has to be made of a transparent material to permit ocular observation. This note describes a similar method in which these drawbacks are avoided as the vapour to be determined need not reach the dew-point, but is instead allowed to come to equilibrium with a probe in the form of a small piece of metal foil with which it forms an alloy.

Consider the sample tube arrangement in Fig. 1. The system consists in this case of an evacuated and closed tube containing the sample in the bottom part and the probe fixed on a hook in the top. The tube is placed in a vertical or nearly vertical position in a furnace to allow the sample to be a melt if necessary. The furnace has two well defined and controlled temperature zones covering the top and the bottom parts of the sample tube. Radiation shields of thin molybdenum metal arranged to avoid radiation from the hotter top to the cooler bottom zone but allowing the vapour to pass freely are placed between the probe and the sample. Indentations in

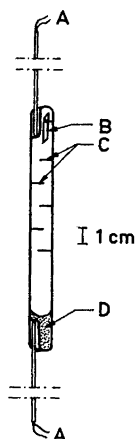


Fig. 1. Sample tube. A. Thermocouple. B. Silver foil. C. Radiation shield. D. Cadmium melt.

the top and bottom of the tube for thermocouples are made to facilitate accurate measurement of the temperature of the probe and the sample.

The method has been used for the measurement of the vapour pressure of Cd in the systems Ag/Cd and Cd/CdCl<sub>2</sub>. In the case of the Ag/Cd system the vapour pressure of Cd above solid alloys at 700°C was determined by investigating the equilibrium composition of the alloy formed when the probe, consisting of a 50 μ thick pure Ag-foil, was kept in an atmosphere of pure Cd-vapour of a known pressure. This was done by keeping the probe in the top constant at 700°C while the temperature of the pure Cd in the bottom was varied at each experiment. When the probe had picked up Cd from the vapour corresponding to equilibrium the sample tube was withdrawn from the furnace and rapidly quenched. As the vapour pressure of pure Cd is accurately known as a function of temperature the variation of Cd-pressure with alloy composition can easily be determined by analysis of the probe. This could be done simply by weighing the probe before and after an experiment. With this knowledge

of the Ag/Cd system the Cd-pressure above Cd/CdCl<sub>2</sub> melts at 600°C could be determined by measuring the equilibrium composition of the probe kept at 700°C and the corresponding composition of the melt at 600°C.

To make sure that equilibrium between the melt and the probe was attained several experiments were conducted, starting with a Cd-content higher than the expected equilibrium composition. The results from these experiments showed that the composition obtained was independent of the side from which the equilibrium was approached.

Blanks showed that no measurable loss of Ag occurred during the time of an experiment. In order to check the method some of the probe alloys were cut in half and analyzed on a Microprobe. From Table 1 it can be seen that the weight %

Table 1. Composition of Ag/Cd alloys according to weighing and microsond analysis in weight %.

Weighing	Microsond
36.25	36.5
37.00	37.0
42.40	42.3
22.90	21.9
22.60	21.6

Cd in the probes obtained from weighing shows very good agreement with the results from the Microprobe analysis in spite of the fact that the latter is not expected to give an accuracy better than ±1 weight %. Results from measurements on the Ag/Cd and on the Cd/CdCl<sub>2</sub> system will be published shortly.

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