A HIGH-TEMPERATURE MANOMETER AND THE DECOMPOSITION PRESSURE OF PYRITE

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The Rodebush low-pressure manometer has been adapted for high temperature use. A precision of the order of 10^{-2} mm Hg is obtained. The factors affecting the precision and the limitation of the method are discussed. The decomposition pressure of pyrite has been measured in the temperature range 500-552°C. In this range the decomposition sulphur pressure may be expressed by the equation:

$$\log p_{Sx} \text{ (atm)} = \frac{-15{,}733}{T} + 16\cdot335\,.$$

As the association of S_2 into larger molecules is insignificant in the temperature and pressure range in question, the above equation gives essentially the partial pressure of S_2.

For the determination of vapour pressures and decomposition pressures at high temperature, various methods exist. For pressures in the range from 10^{-2} atm to several atmospheres the Bodenstein silica spiral manometer has proved very useful. For pressures down to about 10^{-3} atm the dew-point method has also found considerable application. That method is limited, however, to systems where the vapour pressure of the pure volatile component is already known as a function of temperature. In the pressure range below 10^{-4} atm, the Knudsen effusion method is very useful, and for pressures down to 10^{-10} atm, the vapour pressure or decomposition pressure may be estimated by means of Langmuir's method of evaporation rate. The flow method which has been used for a considerable pressure range has many inherent weaknesses such as incomplete saturation of the carrier gas and thermal diffusion in the gas mixture. Finally, the reaction equilibrium with a gas mixture, e.g. of metal sulphides with a hydrogen sulphide + hydrogen mixture, has been used down to extremely low partial pressures of the component in question.

For the intermediate pressure range, from 10^{-5} to 10^{-2} atm a simple method for accurate measurements of vapour pressures at high temperature has been lacking. Several years ago, Rodebush and co-workers [1,2] described a manometer where the force is measured which the gas pressure exerts upon a lid which covers an opening to a high-vacuum system. That method was used to measure the vapour pressure above mixtures of molten halides. The same principle was later used by Deitz [3] and by Balson.[4] The latter used the method to measure the vapour pressure of reactive organic compounds at room temperature. In spite of its inherent advantages, the method has not found any wide application for high temperature work. In the present investigation the method has been modified, and has been used to measure the decomposition pressure of pyrite between 500 and 550°C.

For the decomposition of pyrite into pyrrhotite according to the reaction

$$\frac{2}{1-x}\,\text{FeS}_2 = \frac{2}{1-x}\,\text{FeS}_{1+x} + \text{S}_2(g)\,, \tag{1}$$
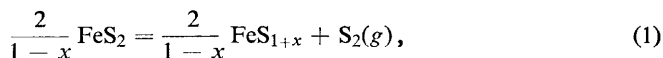
a large number of measurements exist. Allen and Lombard [5] and Rosenqvist [6]

used a dew-point method, whereas the Bodenstein silica spiral manometer was used by D'Or [7] and by Juza and Biltz.[8] Other measurements were made by Raeder [9] and De Rudder.[10] Although most previous measurements agree rather well around 690°C, where the decomposition pressure is 1 atm, there is considerable divergence between the various sets of data around 600 C. Therefore, from measurements of the decomposition pressure at temperatures well below those covered by previous workers the variation of the decomposition pressure with temperature should more accurately be obtained.
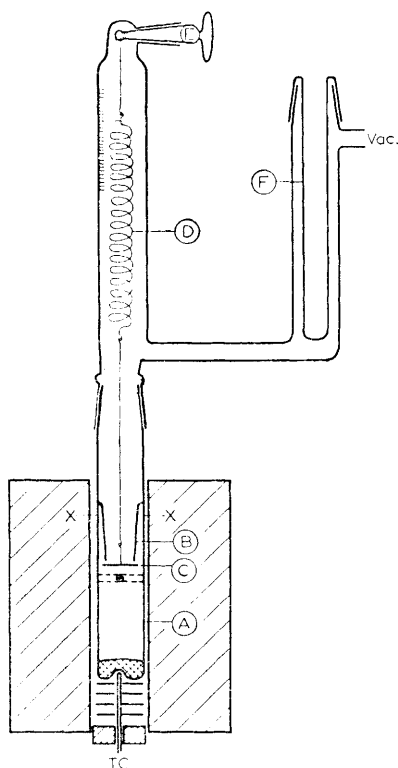

FIG. 1.—Apparatus.

A, silica tube ; B, internal flange ; C, silica disc ; D, Pyrex helix; E, ground joint bobbin ; F, cooling trap with ice or dry ice + alcohol.

EXPERIMENTAL

APPARATUS

The apparatus is shown in fig. 1. It consists of a silica tube A which contains the substance to be studied. This tube has an internal flange B which is ground and polished optically flat. The tube A is connected with the Pyrex parts by means of a ground joint. The flange is covered by an optically flat silica disc C suspended in a silica fibre, which in turn is connected to a Pyrex helix D. The latter is suspended in a nylon thread which is wound around a " bobbin " connected to the movable ground glass joint E. The apparatus is connected to a high-vacuum pump through a cooling trap F, which prevents the volatile component from entering the pump.

The measurements are carried out in the following manner. First, the entire system is evacuated, and the substance may be degassed by gentle heating. By turning the ground joint E, the disc is raised and closes the flange B. The substance is then heated to the desired temperature, and care is taken that the entire closed-off part of tube A is kept well above the dew-point of the volatile component. The pressure now exerts a force on the disc which in addition to the tension in the helix keeps the disc pressed against the flange.

By turning the ground joint E back, the tension in the helix is released, and a point is reached where the disc drops owing to its own weight. This point is easily noticed by the sudden movement in the lower end of the helix. A silica bar prevents the disc from dropping too far. The tension in the helix prior to the drop may now be read by the position of a pointer at the upper end of the helix. Thus a small gas pressure corresponds to a large extension of the helix and vice versa.

The weight of the disc is about 3·33 g and the diameter of the flange about 2 cm, which corresponds to a maximum pressure of about 1 mm Hg. The measuring range is extended further by loading the disc with a silica tube to a total weight of about 6·24 g, which is only a little less than the breaking limit of the helix, 10 g. The measuring range may be extended further by the use of heavier helix gauges, or by a smaller flange diameter.

The apparatus was calibrated against a mercury pressure gauge (Vacustat), which during calibration was connected to the lower part of tube A by connections not shown on fig. 1. After evacuation and closing of the disc C, air was introduced into the lower part of tube A and its pressure was measured with the mercury pressure gauge. By comparing the pressure measured with the position of the upper end of the helix at the point of release of the disc, a calibration curve was obtained which was used for subsequent

measurements. The calibration curve showed that for extensions of the helix up to 200 % of its original length, there was a linear relation between the extension and the pressure under the disc. Only for extensions above 200 % did the calibration curve deviate from a straight line, and the scatter of the calibration points was more pronounced. This anomaly is possibly caused by deviations from Hooke's law and relaxation phenomenon in the glass helix. The largest extensions were obtained by the combination of small gas pressures and a loaded disc. Therefore, for all subsequent measurements, pressures up to about 1 mm Hg were measured with the unloaded disc, and pressures between 1 and 2 mm Hg with the loaded disc. Thus all measurements were carried out in the range of a linear calibration curve.

By separate experiments the helix was loaded with known weights, and the extension was measured. By comparing the readings with the calibration curve the effective area of the disc was calculated. In the present case this was found to be 2·71 cm² as compared to 4·19 cm² for the outer area and 2·35 cm² for the inner area of the flange. The readings were not affected markedly by a slight tilt in the suspended disc, and neither for the calibration nor for the subsequent measurements was any sticking to the polished flange observed.

Readings of the helix extension were obtained with a precision corresponding to less than 0·01 mm Hg by means of a simple lens. The accuracy of calibration was mainly limited by the accuracy of the mercury pressure gauge, and corresponded to 0·01 mm Hg. With the use of a better calibrating instrument and a good telescope the accuracy should be markedly improved.

The method is limited by the leakage past the disc in its closed position and by the rate of vaporization or decomposition of the substance in question. By separate experiments it was found that the leakage past the closed disc amounted to 2 ml of air at 20°C per second, independent of the air pressure. This corresponds to 10^{-4} mole of air per sec per atm. From the kinetic gas theory one may calculate the number n of moles which leaks into a vacuum through a cross-section A' (cm²) per sec equal to

$$n = 44\cdot3 A'p/\sqrt{MT},$$

where p is the pressure in atm and M the molecular weight of the gas. The observed value of $n = 10^{-4}$ gives the cross-section of the leak equal to 2×10^{-4} cm².

In comparison the rate of vaporization is equal to $n_{\text{vap}} = 44\cdot3 Ap°\alpha_v/\sqrt{MT}$; and of condensation $n_{\text{cond}} = 44\cdot3 Ap\alpha_c/\sqrt{MT}$. Here $p°$ denotes the saturation pressure, p the actual pressure in the gas and A the exposed surface area of the substance. α_v and α_c are the vaporization and condensation factors respectively, which are close to one for most normal substances, but may be very much less than one for certain substances with abnormally low vaporization rates (red phosphorus and arsenic).

By steady-state conditions, the relative error due to the leak will be

$$\frac{p_0 - p}{p} = \frac{A'}{A\alpha},$$

where α represents some average of α_v and α_c.

It follows that for all normal substances with α close to one the relative error will be insignificant for an exposed area of the order of 1 cm². It can also be shown that for a tube volume of the order of 100 cm³ virtually steady-state conditions will be established within a fraction of a second. This was ascertained by separate calibration experiments carried out with ice at $-20°$C where the vapour pressure was established inside the closed-off part of the tube A within less than a few seconds, and values in good agreement with literature values were obtained.

This method gives absolute pressure values. By comparison with data obtained by the flow method or the effusion method, the average molecular weight of the vapour can be derived.

MEASUREMENTS ON PYRITE

Two different pyrite preparations were used. One was a natural mineral of high purity. Chemical analysis gave a composition of 53·27 % S and 46·89 % Fe, corresponding to the formula $FeS_{1.97}$. The other was an artificial preparation prepared by heating

weighed amounts of iron powder (*pro analysi*) and redistilled sulphur in evacuated and sealed silica tubes at 700°C. As this reaction is very slow, the partly reacted substance was taken out of the tube, ground and reheated in a new tube for another week. Even this did not give a complete reaction, and the preparation used for the experiments had a composition corresponding to $FeS_{1.78}$, i.e. it was a mixture of pyrite and pyrrhotite.

About 10-12 g of material was used for each series of measurements, the natural pyrite being somewhat coarser ground than the artificial. The measurements were carried out as described above. The attainment of equilibrium was ascertained by repeated readings where the time between each opening of the disc was varied between 2 and 20 min, without this having any effect on the observed pressures. A further check on the attainment of equilibrium was given by the fact that measurements approached from high and low temperature were in good agreement.

A decrease in the observed pressures was observed only when a large part of the pyrite phase had decomposed, and the remaining phase was covered with pyrrhotite. In these cases the observed pressure increased with increasing time between the openings of the disc, and these readings were disregarded. For the natural pyrite the composition at which this first occurred was determined to be $FeS_{1.68}$. For the artificial pyrite the composition was determined after the observed pressure had decreased by about 30 %, and a composition corresponding to $FeS_{1.24}$ was obtained. X-ray examination revealed that even in this case the preparation contained unreacted pyrite phase in addition to pyrrhotite.

After completion of each series of measurements the tube A was cut open around the line *xx* (fig. 1) by means of a diamond saw. The other preparation was put in, and the cut was sealed with a torch. By the use of a smaller side tube this operation should be considerably simplified.

After the end of all measurements the calibration of the apparatus with air was repeated, and no significant changes were observed. Finally, the temperature readings were calibrated against a master thermocouple standardized by the National Physical Laboratories and inserted into the tube A to the position normally occupied by the sample. The temperature readings are regarded as correct to within less than 1°C.

RESULTS

The results are shown in fig. 2. The two pyrite preparations agree well with each other. In addition are given the results of previous investigators in the form of straight lines through their original points.

The present investigation shows that in the temperature range 500-552°C the decomposition pressure of pyrite may be expressed by the equation,

$$\log p_{S_x}(\text{atm}) = (-15{,}733/T) + 16{\cdot}335.$$

In this temperature and pressure range the association of S_2 into S_4, S_6 and S_8 is insignificant,[11, 12] and the above expression may equally well be used for the partial pressure of S_2 above the pyrite + pyrrhotite mixture.

If the logarithmic expression is extended to higher temperatures it agrees well with the average of previous measurements, particularly around 690°C where the decomposition pressure is 1 atm. This indicates that the above expression is valid in the entire temperature range 500-700°C, within the limits of accuracy for the S_2 as well as for the total sulphur pressure. At even higher temperatures and pressures the association of S_2 becomes more pronounced, and the curve for the total sulphur pressure will diverge towards higher values than the curve for the S_2-pressure.

From the observed equation for p_{S_2} the corresponding free energy for eqn. (1) may be derived:

$$\Delta G^\circ = 71{,}970 - 74{\cdot}73\,T\ \text{cal.}$$

As the non-stoichiometry of pyrrhotite, expressed by the value of x in eqn. (1), is a function of temperature, this free-energy expression will have a rather formal value, however.
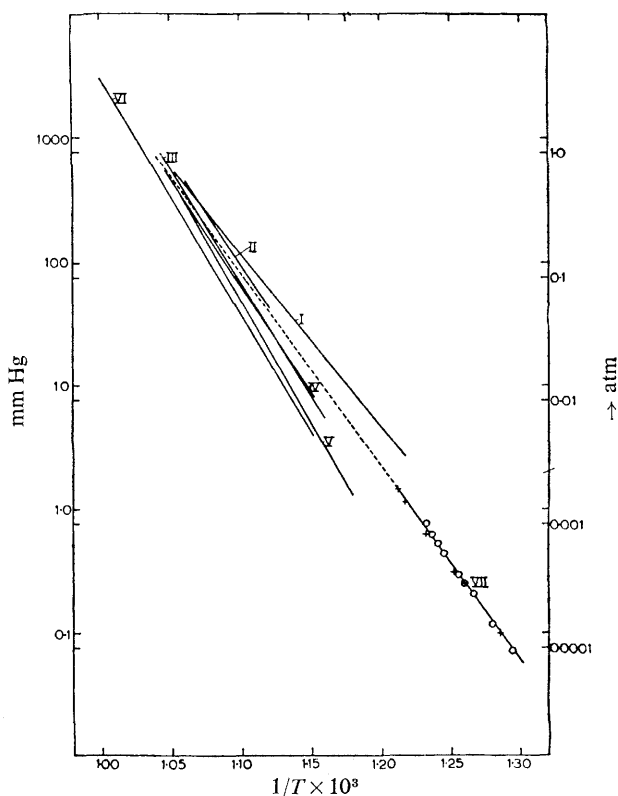
Fig. 2.—Logarithm of sulphur pressure against inverse temperature.

I. D'Or	V. Allen and Lombard
II. Juza and Biltz	VI. Rosenqvist
III. Raeder	VII. this work
IV. De Rudder	

○ synthetic pyrite
+ natural pyrite

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