[Contribution from the Laboratory of Physical Chemistry, University of Wisconsin]

THE VAPOR PRESSURE OF ARSENIC TROXIDE

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Measurements of the vapor pressure of arsenic trioxide up to 500° are presented in this communication. These measurements on the liquid oxide make it possible to draw conclusions concerning the allotropic forms of arsenic trioxide.

The vapor pressure of the solid has been determined before,[1] and all the investigations are in satisfactory agreement, but the work of Welch and Duschak at low temperatures with the air-saturation method is the most complete.

It has been shown by Biltz and others[2] that arsenic trioxide exists in the gas phase as As_4O_6 at temperatures up to 700°. In the solid phase three forms can exist, the octahedral, the monoclinic and the vitreous. Before the work of Welch and Duschak on melting points and previous to the measurements of this investigation, it was not possible to determine all the conditions of stability of the different allotropic forms.

Experimental Procedure

The apparatus is shown in Fig. 1.

The thermostat consisted of an electrically-heated iron pot, filled with tin (65%) and lead (35%) and heavily insulated with asbestos. Temperature regulation was accomplished by adjustment of a reactance coil. The bath could be heated to 800° with 5 amperes at 110 volts. The molten metal was covered with a thick layer of graphite to prevent oxidation and to reduce heat losses from the surface. The Pyrex vessels did not crack when they were set into the molten metal and the graphite kept the metal from sticking to them when they were removed. The apparatus was not cracked even by the freezing of the metal bath.

The temperature was measured with calibrated, copper-constantan thermocouples and a small potentiometer. Since the temperature could not be determined within 1°, it was found unnecessary to stir the bath. Whenever the temperature was changed, it was changed very slowly to avoid thermal lag (5–10° per hour).

In these experiments the Gibson diaphragm[3] was used. A special reference rod was sealed above the pointer to serve as a zero indicator, and the position of the pointer was observed with a microscope. The manometer readings were accurate to about 1 mm. The large bottle served as a reservoir to facilitate small pressure adjustments and to keep the fragile diaphragm from breaking on standing overnight with slight leaks.

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[1] Stelzner, *Dissertation*, Erlangen University, **1901**. Niederschulte, *Dissertation*, Erlangen University, **1903**. Welch and Duschak, *Bur. Mines Techn. Paper*, **81** (1917). Smellie, *J. Soc. Chem. Ind.*, **42**, 466 (1923).

[2] Biltz, *Z. physik. Chem.*, **19**, 417 (1896). Scott, *Proc. Roy. Soc. Edinburgh*, **14**, 410 (1887).

[3] Gibson, *Proc. Roy. Soc. Edinburgh*, **23**, 1 (1912). Jackson, *J. Chem. Soc.*, **99**, 1066 (1911).

Experimental Results

Four determinations were made, the first two of which were concerned only with the melted form. The third extended from 225° to 520° but the diaphragm became distorted at the higher temperature.

The fourth determination was made on arsenic trioxide which had been prepared by subliming Merck's product. The first part of the sublimate was discarded because it was tinged a faint red, but the rest of the material consisted of pure, clear, octahedral crystals. Seven g. was placed in the flask, partly immersed in the thermostat, and evacuated for an hour at 327° to insure complete melting of the crystals and removal of the adsorbed air. While evacuating the flask, it was necessary to evacuate the manometer at the same rate to avoid breaking the diaphragm.

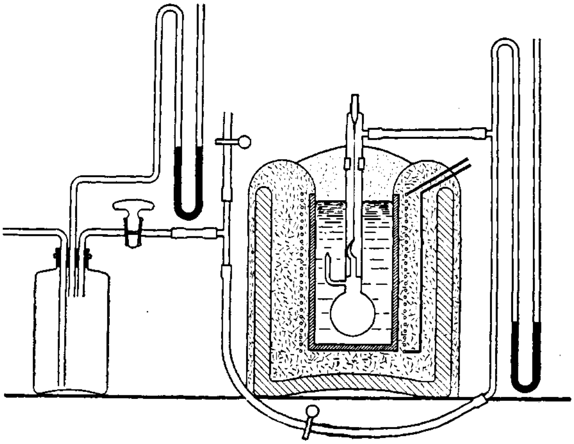

Fig. 1.—Apparatus for measuring the vapor pressure of arsenic trioxide.

After the apparatus had been sealed off and lowered into the thermostat, the pressure rose for the first half hour, as the temperature was increased, and then fell to 111 mm. at 339°, after which it continued to rise in a normal manner. The high values obtained at first were undoubtedly due to the presence of crystals which deposited in the upper part of the bulb during evacuation, and melted only after the apparatus had been immersed in the thermostat for some time.

The temperature was increased at first to 338° and then lowered gradually to 218°, at which temperature the vapor pressure is so low that it cannot be measured with the apparatus. Further reduction in temperature gave no change in the reading of the diaphragm. These tests showed that all the air had been removed and that the zero point had not been changed by heating to 388°.

When the temperature was raised the pressure readings were higher than for the corresponding temperature on cooling. When 293° was passed the pressure curve dropped off slightly, remained fairly constant for a time and at about 315° joined the curve which was obtained on cooling.

This decrease in vapor pressure with an increase in temperature is similar to the case of sulfur trioxide reported by Smits.[4] In both cases two allotropic solids and a liquid are involved.

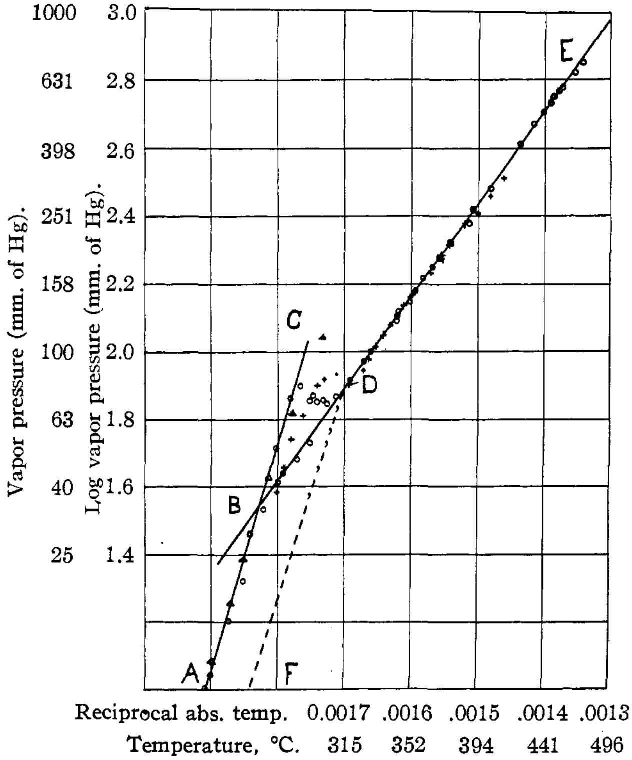

Fig. 2.—The vapor pressure of arsenic trioxide. FD is drawn from D so as to intersect ABC at 100°, at which temperature Welch and Duschak found the octahedral arsenic trioxide still changing to the monoclinic.

+—Third determination.	ABC—Octahedral.
○—Fourth determination.	BDE—Liquid.
△—Data of Stelzner.	FD—Monoclinic (calculated).

The experimental measurements are summarized in Fig. 2, and it is seen that the results on the octahedral arsenic trioxide check closely, at the lower temperatures, with those of other investigators.

The curve for the vapor pressure of the liquid arsenic trioxide can be expressed by the equation $\log P = -(2722/T) + 6.513$. It holds for any

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[4] Smits, *J. Chem. Soc.*, **125**, 2554 (1924).

sample of arsenic trioxide above 315°, and it is reliable down to 275° for arsenic trioxide which has been recently cooled from temperatures above 315°.

The curve for the vapor pressure of the octahedral arsenic trioxide corresponds to the equation $\log P = -(6670/T) + 13.728$. This form is unstable but its rate of transition is so slow that the equation represents quite well the vapor pressure of ordinary solid arsenic trioxide (octahedral) at temperatures up to about 250°, or higher, depending on the rate of heating.

At temperatures somewhat below 315°, arsenic trioxide which has been raised from a lower temperature has an indefinite pressure depending on the extent of the transition to the more stable monoclinic variety. The two allotropic forms appear to give solid solutions.

These simple equations are recognized as approximate equations but the experimental points seem to lie on the straight lines within the limit of accuracy of the experimental data. The least accurate factor is probably the determination of the true temperature of the solid or liquid.

An attempt was made to study the transitions through thermal analysis, but no break in the cooling or heating curves could be found when a thermocouple was placed in a mass of the crystals. It is probable that the transition was too slow to permit the use of this method.

Conclusions

The line ABC gives the vapor-pressure curve for the octahedral arsenic trioxide (the logarithm of the vapor pressure plotted against the reciprocal of the absolute temperature). The line BDE gives the vapor pressure of the liquid arsenic trioxide. The two intersect at the point B, corresponding to a temperature of 275°. This is the melting point of the octahedral arsenic trioxide, for both liquid and octahedral forms are in equilibrium at this temperature. Welch and Duschak, using microscopical tests, set the melting point provisionally at 251°. The method outlined above would seem to be more accurate, since it is free from complications caused by the octahedral crystals passing over into the monoclinic form.

The line FD is a *provisional* line representing the vapor pressure of monoclinic arsenic trioxide. No direct measurements of this quantity have been made but the dotted line gives the best information now available. Welch and Duschak found that the monoclinic variety melts at 313°, and this temperature is checked by the present data. The erratic vapor pressures of the heated solid disappear at temperatures above 315° (Fig. 2), and the sudden regularity must be due to complete liquefaction. At about 315°, then, the monoclinic and liquid forms are in equilibrium and their vapor-pressure curves, FD and BDE, must intersect and fix the point D.

The logarithm of the vapor pressure of monoclinic trioxide plotted against the reciprocal of the absolute temperature should give a line which is nearly straight, and one other point in addition to the point D is sufficient to determine the line FD. Such a point is found in the transition temperature of the octahedral to the monoclinic, for at this temperature the two vapor pressures are equal, and the lines CBA and DF must intersect. This temperature is not known accurately, but Welch and Duschak found that it must be as low as 100°. Fortunately, the extrapolation to 100° is so great that a considerable error in the exact location of this transition does not affect appreciably the slope of the dotted line. The equation for this provisional line is $\log P = -(6100/T) + 12.26$.

The lines in Fig. 2 give the conditions of stable equilibrium, but in predicting the behavior of any chemical system it is not sufficient to consider only factors of equilibrium, for the time variable must also be considered. In this connection Welch and Duschak recorded an important observation. They found that the octahedral crystals grow rapidly but that the monoclinic grow very slowly. This fact explains the sluggishness with which the monoclinic variety is formed when the equilibrium conditions are favorable, and explains also the ready formation of the octahedral variety from vapor, liquid or supercooled liquid.

Fig. 2 shows that the vapor pressures fall on the line BD when the liquid is cooled below the freezing point of the monoclinic, but they change over to the line ABC when the freezing point of the octahedral is passed. If the transition of the liquid to the monoclinic proceeded with any appreciable velocity, some of the points would fall below DB toward DF. There is little tendency for the unstable octahedral form to pass over to the stable monoclinic until temperatures above approximately 250° are reached, although it is probable that if the heating were carried out much more slowly, some of the points would fall away from ABC toward FD at still lower temperatures. The octahedral form should melt at 275°, but it does not melt completely because, at this temperature, some of it has changed to the monoclinic variety with a higher melting point. The two forms appear to give solid solutions with vapor pressures depending on the composition.

When the vapor is condensed at temperatures below 275° the rapidly growing octahedral trioxide is formed in preference to the monoclinic, although the latter is more stable. When the vapor is condensed above 315° the liquid phase is produced. When it is condensed below 315° and above 275°, where the octahedral cannot be formed, there is a chance of obtaining monoclinic crystals.

The vitreous variety, however, may be formed in preference to the monoclinic or even to the octahedral. Although the monoclinic form is more stable than the octahedral or the vitreous over the temperature range investigated, the transition is so slow that no crystallographic evidence of the monoclinic form could be obtained in these experiments. Welch and Duschak found that the speed of transition was accelerated greatly by water. In the present experiments water was quite thoroughly removed by continued evacuation at about 325°.

The molar heats of vaporization of the different allotropic forms may be calculated at the temperatures studied with the help of the Clausius-Clapeyron equation. The calories absorbed in vaporizing 1 g. of the arsenic trioxide are obtained by dividing the molar heat of vaporization by the molecular weight of the vapor (396). The values are as follows: liquid, 31.5; octahedral, 77.1; monoclinic, (71, estimated). By subtraction, the heats of fusion and transition may be calculated as follows: octahedral ⟶ liquid, 45.6; monoclinic ⟶ liquid, (39, estimated); octahedral ⟶ monoclinic, (6, estimated).

Summary

1. The vapor pressures of octahedral and liquid arsenic trioxide have been measured at high temperatures and the equations have been determined. The vapor pressure of monoclinic arsenic trioxide has been estimated.

2. The melting point of the octahedral form was found to be 275°, and that of the monoclinic *approximately* 315°.

3. The heats of vaporization, fusion and transition have been calculated.

4. The regions of stability of the various allotropic forms of arsenic trioxide have been determined and the influence of the time variable has been discussed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE POLYMERIZATION AND HYDROGENATION OF ETHYLENE BY MEANS OF EXCITED MERCURY ATOMS

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In 1910, Berthelot and Gaudechon[1] demonstrated the chemical effect of ultraviolet light on a number of reactions. Among the reactions studied were those of the polymerization of ethylene and acetylene. It is to be remarked that in these experiments, mercury vapor was present in the reaction chamber since the authors state that a solid was quickly deposited on the surface of the mercury. The importance of this small amount of mercury vapor was emphasized by the work of Cario and Franck[2]

[1] Berthelot and Gaudechon, *Compt. rend.*, **150**, 1169 (1910).

[2] Cario and Franck, *Z. Physik*, **11**, 161 (1922).