



Fermi National Accelerator Laboratory

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Measurement of TMAE and TEA Vapor Pressures*

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Abstract

A new measurement of the vapor pressure of the photosensitive gas TMAE as well as a measurement of the vapor pressure of TEA is presented.

1. Introduction

The photosensitive gases terakis(dimethylamino)ethylene, TMAE, and triethylamine, TEA, have been used for many years in such applications as Cherenkov ring imaging and to detect the scintillation light from gas scintillation proportional counters (see ref.1 for a review of the subject). Because TEA has a substantial vapor pressure at room temperature, its concentration is usually adjusted to be considerably less than the saturated concentration. TMAE, on the other hand, has a very low vapor pressure and therefore is normally used at the highest pressure allowed by the operating temperature of the instrument and the surrounding environment. Thus it is important to know the functional form of the vapor pressure of TMAE so that the concentration can be accurately controlled.

From the very introduction of TMAE to the field of instrumentation, it was realized that the published vapor pressures were incorrect. The published pressures[2] were off by factors of about 60 and 20 at temperatures of 30 °C and 90 °C, respectively. Because of the obvious discrepancy between the published and the observed pressures, this was one of the first quantities measured by this author in the evaluation of TMAE.

The vapor pressure of TMAE was expected to obey the Clausius-Clapeyron equation:

$$P = P_0 \exp \left[\frac{\Delta H}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right], \quad (1)$$

where P_0 and T_0 are references pressure in torr and temperature in Kelvin. ΔH is the molar heat of vaporization and R is the molar gas constant. Fitting the data to the Clausius-Clapeyron equation, the functional form of the vapor pressure was determined to be[3]:

$$P_{\text{old}} = 0.577 \exp \left[6454 \left(\frac{1}{300} - \frac{1}{T} \right) \right], \quad (2)$$

where the pressure P is in torr and T is the temperature in Kelvin. The value $T_0 = 300$ K was chosen for convenience.

This early measurement was made with a small sample of material, purified as well as was possible at the time. Because of the very low vapor pressure of TMAE, the pressure is very sensitive to any contamination of the material. With improvements in purification techniques, small disagreements to the value reported above began to be reported. We have therefore made a new evaluation of the TMAE vapor pressure.

In a search of the literature, we have only been able to find the vapor pressure of TEA for three temperatures, which cannot be fitted with the Clausius-Clapeyron equation. We have therefore made a measurement of the vapor pressure of TEA which is reported here.

2. Material Preparation

Over the last few years, a great deal of effort has been made in learning how to work with TMAE. Besides the fact that it reacts with oxygen, it also reacts with many other materials such as rubber. Therefore, even TMAE fresh from the supplier must be purified before use. There are three important steps in the purification of TMAE: washing, drying, and final purification.

The TMAE is washed in the following manner: Under nitrogen, the TMAE is shaken with a small portion of deoxygenated water in a separating funnel. (The oxygen has first been removed from the water by bubbling nitrogen or argon through it for 12 hours.) The water is then removed and the procedure is repeated until the water is clear. This step removes the oxidation products of tetramethyl oxamide, tetromethyl urea, and dimethyl amine. This step noticeably lightens the color of the TMAE.

The TMAE is then dried by storing it in tightly closed bottles containing 4Å or 5Å molecular sieve. The oxygen has been removed from the molecular sieve by evacuation and then back-filling with dry nitrogen. For most applications, the TMAE is now ready for use.

The final purification was performed by vacuum distilling the TMAE (at 50 °C) onto a mixture of molecular sieve and activated alumina that has been outgassed under vacuum at about 400 °C for several hours. The first and last fractions of the TMAE are discarded in the distillation step.

It should be noted that whenever working with TMAE with a vacuum system, a liquid nitrogen cold trap should be used. The TMAE will react with the seals in the pump, and cause them to deteriorate in a very short time.

The TEA used was reagent grade. The purification consisted of only the vacuum distillation step described above. About the first and the last 10% of the material were discarded. The last fraction had a noticeable amber tint to it, while TEA itself is a clear liquid.

3. Measurement Procedure

The sample of TMAE or TEA to be measured was kept at a constant temperature by a circulating water bath, while the temperature was read with a thermometer that was marked in units of 0.2 °C. The pressure was read with a calibrated Barocel pressure sensor

(Datametrics) with a full range of 100 torr. Since some of the measurements were made with the TMAE above room temperature, all measurements were made in an oven kept at least 10 °C above the TMAE temperature.

It was found in the measurements of the vapor pressure of TMAE that even though the material was very pure and kept in a clean environment, reproducible results could not be obtained without periodically pumping on the sample to remove some high-pressure contaminant. Therefore, the sample was exposed to a vacuum for several minutes each day. The vacuum was supplied by an ordinary rotary oil pump (ballast open to remove any trace vapors) and a liquid-nitrogen trap.

4. Vapor Pressures

Figures 1 and 2 show the vapor pressure as a function of the reciprocal of the absolute temperature for TMAE and TEA, respectively. The temperature in °C is also shown. The best fit of the TMAE data to the Clausius-Clapeyron equation is:

$$P_{\text{TMAE}} = 0.500 \exp \left[6372 \left(\frac{1}{300} - \frac{1}{T} \right) \right]. \quad (3)$$

This yields a vapor pressure at room temperature (20 °C) of 0.304 torr, whereas eqn. (2) gave a value of 0.349 torr. This is a reduction in the value of 13%.

Figure 1 also shows the old and values of the vapor pressure of TMAE, as well as four data points taken from the literature[4]. The small discrepancy between these four data points and the fit are not considered significant since the least significant figure is 0.01 torr.

The best fit to the TEA data is:

$$P_{\text{TEA}} = 73.2 \exp \left[4299 \left(\frac{1}{300} - \frac{1}{T} \right) \right]. \quad (4)$$

Figure 2 also includes two values of the vapor pressure taken from the literature[5,6]. It should be noted that the boiling point ($P = 760$ torr) given by eqn. (4) is 85.4 °C. The value given for the boiling point of TEA is given as 89.3 °C in the literature[7].

5. Discussion

There has recently been a measurement made[8] that confirms the old TMAE vapor pressure given by eqn. (2). We believe that this reflects a small amount of contamination in the sample studied. Since TMAE has such a small vapor pressure, it requires a very small amount of contaminant with a high vapor pressure to substantially increase the measured

pressure. In a mixture, the pressure of the contaminant is equal to the vapor pressure of the material times its mole fraction (Raoult's rule). Thus, at 20°C a concentration of only 36 ppm of dimethyl amine (a known contaminant in TMAE) would account for the difference in the old and new fits to the vapor pressure. Henry's law states that for nonpolar solvents, such as TMAE, the mole fraction of solute is proportional to its vapor pressure. Thus, such a contaminant as dimethyl amine, which has a vapor pressure of about 1260 torr at 20 °C, should have a very high solubility.

Another consequence of Raoult's rule is that since TMAE is by far the majority material in any sample studied, any noticeable effect of a contaminant on the vapor pressure will be to increase the pressure. Therefore, an erroneous measurement, barring systematic problems, will tend to be too high.

References

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Figure Captions

- Figure 1 TMAE vapor pressure as a function of the reciprocal of the absolute temperature and as a function of the temperature in °C. The old value is also shown. The four data points labeled A are taken from ref.4.
- Figure 2 TEA vapor pressure as a function of the reciprocal of the absolute temperature and as a function of the temperature in °C. The two data points labeled A and B are taken from ref. 5 and 6, respectively.

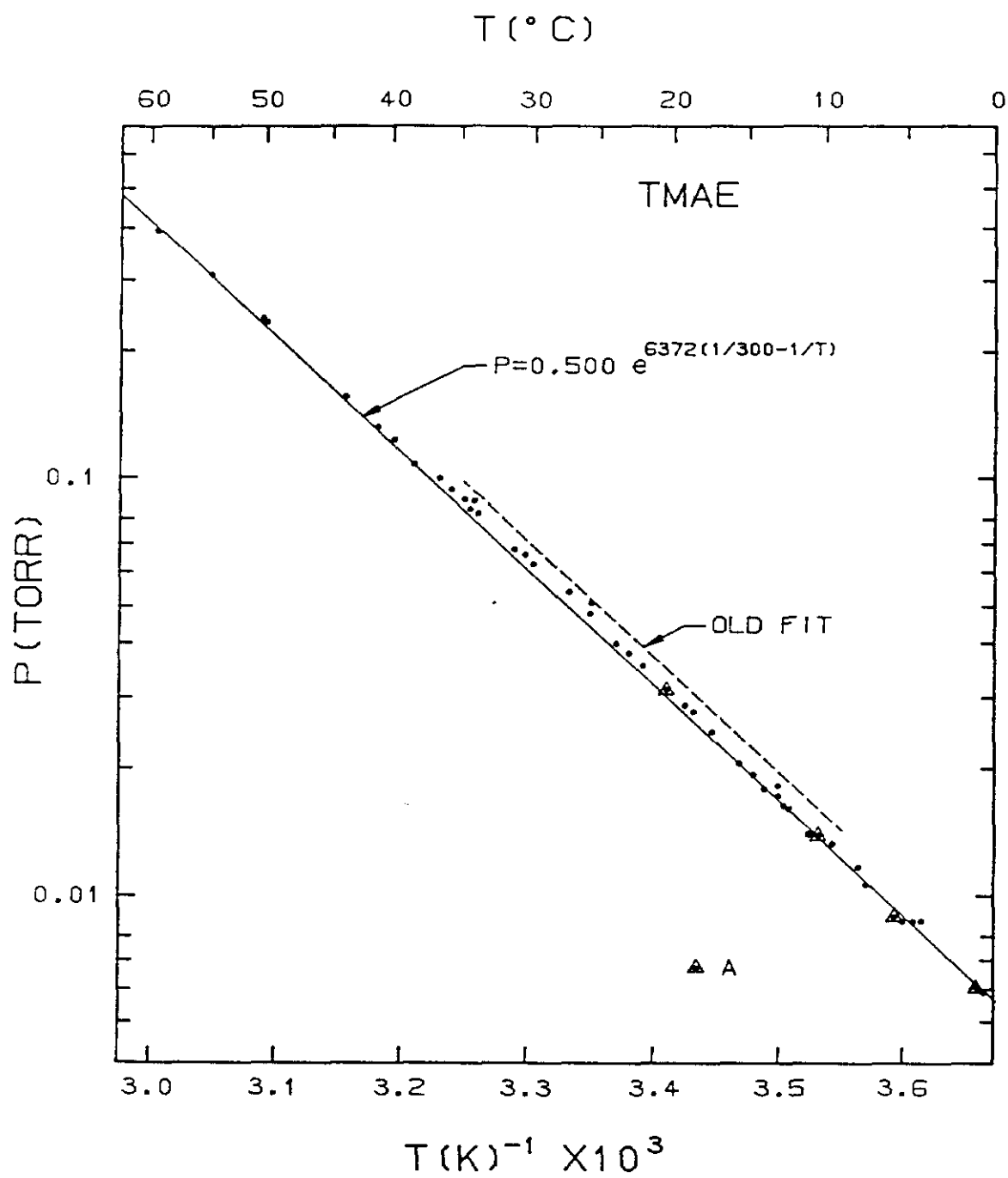


Figure 1

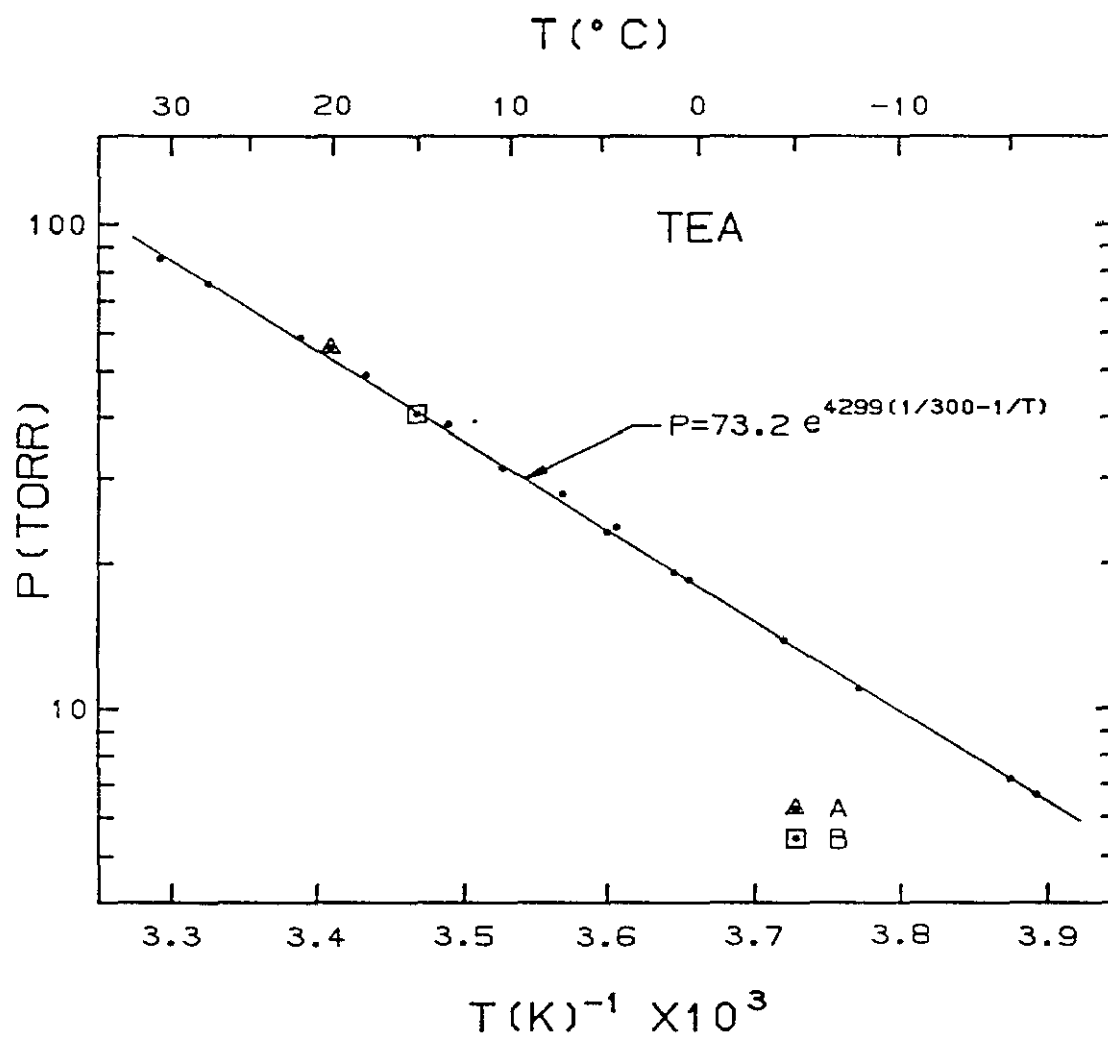


Figure 2