

Using Vapors with the AutoChem

This tech tip will describe how to use Micromeritics' AutoChem Series analyzer when equipped with a vapor generator. Vapor probes are used often to expand the understanding of the surface properties of materials, and catalyst researchers use organic amines routinely to probe the acidity of zeolites. These compounds require the use of a vapor generator. The Micromeritics AutoChem Series features an optional vapor generator that employs a temperature-controlled valve, reflux condenser, and flask for the probe liquid. The temperature control of these components allows precise control of the vapor composition. The Antoine vapor-pressure correlation is useful for determining the appropriate settings for the vapor generator temperature zones, and also calculating the active concentration of the vapor in the AutoChem loop.

Instrument settings for use with vapors

Calculating vapor composition

The Antoine vapor-pressure correlation (also referred to as the Antoine equation) and Dalton's law of partial pressures may be used to determine the active concentration of the vapor in the AutoChem loop. The Antoine Vapor-Pressure Correlation is given in equation 1

$$\log_{10} P_v = A - \frac{B}{T + C} \quad (1)$$

where A , B , and C are constants that may be readily obtained for many materials, and T is the temperature of the vapor generator's reflux condenser in Kelvin.

The Antoine vapor-pressure correlation does not have a theoretical basis, but is a powerful tool for fitting vapor pressure data. If $C=0$, the Antoine correlation becomes the Clapeyron equation.

The active concentration of the vapor in the reflux condenser or loop is determined by using the calculated vapor pressure and Dalton's Law of Partial Pressures, equation 2

$$P_T = P_1 + P_2 + P_3 + \dots + P_i \quad (2)$$

where P_T is the total system pressure and P_i is the pressure of each vapor. For dynamic chemisorption applications the loop pressure is used as the total system pressure and can be taken as atmospheric pressure. Also, most vapor adsorption experiments use a binary mixture of a carrier gas (typically helium) and the vapor probe molecule. Equation 2 may be rewritten for the simpler binary gas system, equation 3.

$$P_L = P_v + P_{He} \quad (3)$$

where P_L is the loop pressure, P_v is the partial pressure of the vapor probe, and P_{He} is the partial pressure of helium in the loop. The active concentration (in mole %) of the vapor in the loop, C_i of each vapor (or gas) component is then calculated from equation 4

$$P_v = \frac{C_i}{100\%} P_L \quad (4)$$

A simple rearrangement of equation 4 is then used to determine the active concentration of the vapor.

$$C_i = 100\% \times \frac{P_v}{P_L} \quad (5)$$

Estimating temperature zone settings

The temperature zones for the AutoChem should be altered to reflect the use of vapors in the system and, in particular, the temperature of the valves in the AutoChem should be set to 110 °C to prevent condensation. The AutoChem's vapor generator features a dual zone design. Temperature control of the liquid reservoir (flask) is achieved with a heating mantle and is designed to generate the vapor. The liquid should not be allowed to boil in the liquid reservoir. The AutoChem is also equipped with a reflux condenser, and the temperature of this zone controls the vapor pressure (and concentration of the vapor in the loop). It is a good rule of thumb to set the temperature of the liquid flask 5 – 10 °C above the temperature of the reflux condenser while maintaining the flask temperature below the boiling point of the liquid. The Antoine correlation may be rearranged to a more convenient form for calculating the temperature for a given vapor pressure, equation 6.

$$T = \frac{B}{A - \log_{10} P_v} - C \quad (6)$$

Antoine constants for several vapors that are used commonly are listed in Table 1. These constants are valid for the temperature range defined by T_{min} and T_{max} , and the vapor pressure is in bar.

Example calculations for pyridine

Pyridine adsorption is used often to characterize the acidity of zeolites. The instrument parameters (temperature zone settings) and active concentration of pyridine in the loop (and vapor generator) can be determined easily using the Antoine correlation and Dalton's Law. You can specify an active concentration (C_i) of 10% in the loop, 760 mmHg for the loop pressure (P_L), and then use equation 4 to calculate the vapor pressure of pyridine.

$$P_v = \frac{C_i}{100\%} P_L = \frac{10\%}{100\%} \times 760 \text{ mmHg} = 76 \text{ mmHg}$$

The reflux temperature is then calculated from the vapor pressure of the pyridine using equation 6.

$$T = \frac{B}{A - \log_{10} P_v} - C = \frac{1371.358}{4.1627 - \log_{10} \left(\frac{76}{760} \right)} - (-58.49460) = 324.12 \text{ K}$$

The reflux zone temperature is then calculated from the previous result.

$$T_{reflux} = T - 273.15 K = 324.12 K - 273.15 K = 50.99 \text{ }^{\circ}C$$

The AutoChem reflux zone temperature should be set to **51 °C**.

We can now use a simple rule of thumb to determine the flask temperature

$$T_{flask} = T_{reflux} + 10 \text{ }^{\circ}C = 50.99 \text{ }^{\circ}C + 10 \text{ }^{\circ}C = 60.99 \text{ }^{\circ}C$$

The AutoChem flask zone (boil zone on the AutoChem 2910) temperature should be set to **61 °C**.

The active volume of pyridine in a 0.5-cm³ loop may also be calculated easily from the active concentration (C_i).

$$V_L^A = V_L \times \frac{T_{STD}}{T_{Loop}} \times \frac{P_{Loop}}{P_{STD}} \times \frac{C_v}{100\%} = 0.5 \times \frac{273.15 K}{383.15 K} \times \frac{760 \text{ mmHg}}{760 \text{ mmHg}} \times \frac{10\%}{100\%} = 0.035645 \text{ cm}^3$$

Table 1: Antoine constants for vapors that are commonly used in catalyst research and adsorption studies. The Antoine-Vapor Pressure Correlation is given by $\log_{10} P_v = A - B/(T+C)$, with P_v in bar and T in kelvin

	A	B	C	T _{min}	T _{max}
Acetone	4.4245	1312.2530	-32.4450	259.2	507.0
Benzene	4.0305	1211.0300	-52.3600	280.0	377.0
n-Propanol	5.3138	1690.8640	-51.5040	292.4	370.4
i-Propanol	5.2431	1580.9000	-53.5400	273.0	374.0
i-Propanol	4.8610	1357.4270	-75.8140	329.2	362.1
n-Propyl Amine	4.0717	1108.2000	-49.1500	235.0	350.0
i-Propyl Amine	4.2315	1121.5000	-40.1500	239.0	337.0
Pyridine	4.1627	1371.3580	-58.4960	340.4	426.0
Toluene	4.0787	1343.9430	-53.7730	308.5	384.7
Water	5.0740	1657.4000	-46.1300	284.0	441.0
o-Xylene	4.1238	1474.6700	-59.4600	305.0	445.0
m-Xylene	4.1339	1462.2600	-58.0400	300.0	440.0
p-Xylene	4.1455	1474.4030	-55.3770	286.0	452.4

Antoine Constants Conversions

The AutoChem 2920 (starting with version 2.0) software has been expanded to include the use of Antoine Vapor-Pressure Correlation, and the vapor calibration has been updated to use this correlation. The Options menu includes a Vapor Defaults item and allows the user to specify Antoine constants. The Vapor defaults table will contain the Antoine constants listed in Table 1 for new (or clean) installations of the software. However, users that upgrade from version 1.x of the AutoChem 2920 to version 2.0 (or later releases) must enter these constants. This table is intentionally left blank for upgrades to preserve any user-defined parameters. Antoine constants for vapors not listed in the vapor defaults may be obtained from several sources [1, 2].

The Antoine equation used for estimating the vapor pressure of liquids as a function of temperature as given in equations 7 and 8. Equation 7 is used to calculate the vapor pressure in bar (pressure units), and the AutoChem 2920 software application requires these units for the Antoine Vapor-Pressure Correlation.

$$\log_{10}(P_{bar}) = A_{bar} + \frac{B_{bar}}{T - C} \quad (7)$$

$$\ln(P_{mmHg}) = A_{mmHg} + \frac{B_{mmHg}}{T - C} \quad (8)$$

The Antoine correlation as presented in equation 8 yields vapor pressure in units of mmHg. The Antoine constants A and B are dependent upon the units of pressure (mmHg or bar) and to the logarithmic function that is employed (natural logarithm or base-10 logarithm). However, the Antoine constants are easily converted to either form of logarithm or pressure units. To convert from the traditional mmHg and natural logarithm function we combine equations 7 and 8.

$$e^{\ln(P_{mmHg})} = k \times 10^{\log_{10}(P_{bar})} \quad (9)$$

$$k = 750.0615613 \text{ mmHg/bar} \quad (10)$$

Equation 9 is expanded using the Antoine Correlation and now provides vapor pressures in bar calculated from mmHg-based A and B constants.

$$e^{\left(A_{mmHg} + \frac{B_{mmHg}}{T - C}\right)} = k \times 10^{\log_{10}(P_{bar})} \quad (11)$$

Equation 11 is then simplified using the base-10 logarithm.

$$\left(A_{mmHg} + \frac{B_{mmHg}}{T - C}\right) \log_{10}(e) = \log_{10}(k) + \log_{10}(P_{bar}) \times \log_{10}(10) \quad (12)$$

Rearranging equation 12 and substituting for the pressure conversion factor k we obtain:

$$\left(A_{mmHg} + \frac{B_{mmHg}}{T - C}\right) \times 0.43429 = 2.8751 + \log_{10}(P_{bar}) \times 1 \quad (13)$$

Equation 13 is then rearranged to the familiar form of the Antoine vapor-pressure correlation.

$$\log_{10}(P_{bar}) = \left(A_{mmHg} + \frac{B_{mmHg}}{T - C}\right) \times 0.43429 - 2.8751 \quad (14)$$

$$\log_{10}(P_{bar}) = (0.43429 \times A_{mmHg} - 2.8751) + \left(0.43429 \times \frac{B_{mmHg}}{T - C}\right) \quad (15)$$

The Antoine vapor-pressure constants can now be readily converted from mmHg and natural logarithm base to pressure units of bar and base-10 logarithm.

$$A_{bar} = 0.43429 \times A_{mmHg} - 2.8751 \quad (16)$$

$$B_{bar} = 0.43429 \times B_{mmHg} \quad (17)$$

$$C_{bar} = C_{mmHg} \quad (18)$$

Example calculations for methanol

The Antoine vapor-pressure constants for methanol are given in Table 2 from Prausnitz [1].

These constants can be converted to a form that is suitable for the AutoChem 2920 Vapor Defaults table. An example vapor pressure curve is shown in Figure 1, and demonstrates the equivalency between the original constants and converted constants.

$$A_{bar} = 0.43429 \times A_{mmHg} - 2.8751 = 0.43429 \times 18.5875 - 2.8751 = 5.1973$$

$$B_{bar} = 0.43429 \times B_{mmHg} = 0.43429 \times 3626.55 = 1575.0$$

$$C_{bar} = C_{mmHg} = -34.29$$

Table 2: The Antoine-Vapor Pressure Correlation is given by $\ln(P_v) = A - B/(T+C)$, with P_v in mmHg and T in Kelvin.

	A	B	C	T_{min}	T_{max}
Methanol	18.5875	3626.55	-34.29	257	364

Table 3: The Antoine-Vapor Pressure Correlation is given by $\log_{10}P_v = A - B/(T+C)$, with P_v in bar and T in Kelvin.

	A	B	C	T_{min}	T_{max}
Methanol	5.1973	1575.0	-34.29	257	364

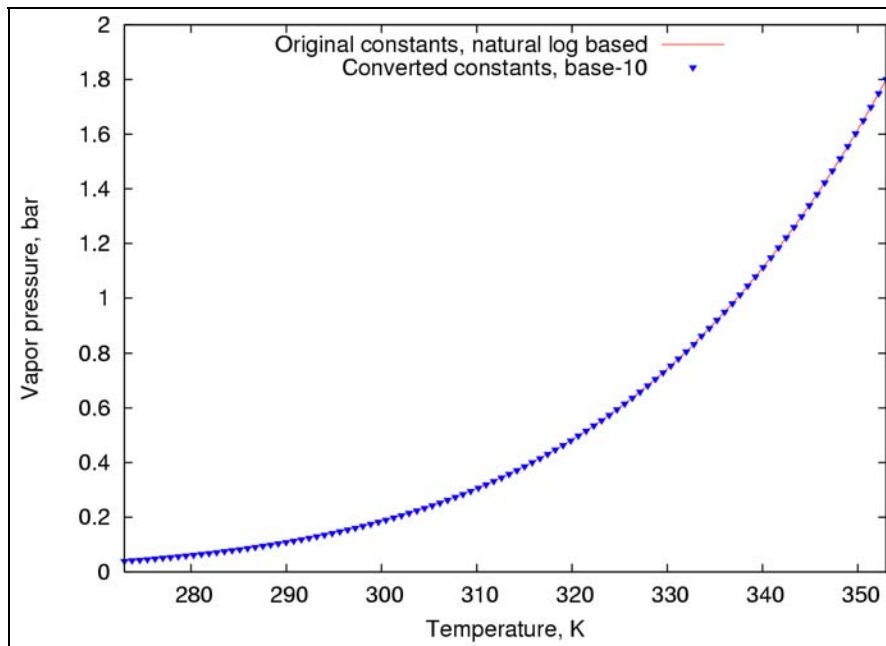


Figure 1: Methanol vapor pressure curve

References

- [1] Robert C. Reid, John M. Prausnitz, and Thomas K. Sherwood, *The Properties of Gases and Liquids*, Third Edition, Appendix A, McGraw-Hill Book Company, New York, 1977
- [2] NIST Chemistry WebBook, <http://webbook.nist.gov/chemistry/>

Additional Articles of Interest

Micromeritics Product Bulletin No. 83, Vapor Generator for AutoChem

Micromeritics Application Note No. 116, Accuracy of Vapor Dosing with the AutoChem