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Aerosol Report

# VAPOR PRESSURE MEASUREMENTS FOR AEROSOL PRODUCTS

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# Vapor Pressure Measurements for Aerosol Products

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The vapor pressures of aerosol products is a subject that has been of interest to the aerosol industry for many years. Not only is it a factor involved in other aerosol properties, such as spray characteristics, flammability, and rate of discharge, but it is also an aerosol property which is subject to governmental regulations.

It has been recognized for a long time that in order to obtain an accurate measurement of the pressure of an aerosol product it is usually necessary to prepressurize the gage with an inert gas, such as air or nitrogen. The reason for this is that practically all aerosol products contain air. The total pressure in these products is equal to the pressure of the aerosol formulation plus the pressure of the air. Loss of air from the aerosol container during a pressure measurement would result in an erroneous measurement and this is avoided by prepressurizing the gage to approximately the same pressure as that in the aerosol container. The method of determining the pressure of aerosol products with a prepressurized gage has been described in detail in a previous publication.[1]

However, in many cases vapor pressure measurements are taken without prepressurizing a gage, either because of a lack of the proper equipment or because of a desire to save time. The significance of vapor pressure measurements taken with a nonprepressurized gage has never been clarified. If the pressure of an aerosol containing air is taken with a gage at a lower pressure than that in the aerosol container, the vapor phase of the aerosol will expand into the gage until the pressure in the gage and the aerosol are equal. The pressure of the propellant in the vapor phase remains essentially constant during expansion into the gage (neglecting any cooling from expansion) since liquefied propellant will vaporize to replace that lost by expansion into the gage. However, in most cases, the pressure due to air will change during the expansion. The ultimate pressure recorded on the gage, therefore, is not the same as the pressure originally present in the aerosol container.

Theoretically, there are two diametrically different processes that can occur when the vapor phase of an aerosol expands into a gage at a lower pressure. These two processes give different pressures. In the first theoretical process (Process 1), the vapor phase of the aerosol container is assumed to mix completely with the air in the gage during the expansion, so that the final composition of the vapor phase in the aerosol container is the same as that in the gage. Depending upon the relative volumes and concentrations of air in the vapor phase of the aerosol and the gage, the final pressure could either be higher, lower or the same as that originally present in the aerosol.

In the second possible process (Process 2), it is assumed that the expanding vapor phase of the aerosol does not mix with the air in the gage but merely compresses the air. Under these conditions, the air in the gage acts only as a piston for the transmittal of pressure to the gage. The pressure will always decrease if Process 2 takes place, because the air pressure in the vapor phase of the aerosol will decrease as a result of the expansion into the gage.

Equations have been developed so that the pressures can be calculated for both Process 1 and Process 2. It is the purpose of this work to compare the experimentally determined pressures obtained when an aerosol expands into a gage at a lower pressure with the pressures calculated for the two different processes and thus determine which of the processes actually takes place.

## Discussion

In order to simplify the following discussion, it is assumed that the pressure of the air in the vapor phase of the aerosol container is greater than that in the gage, and that the volume of the gage is less than the volume of the vapor phase of the aerosol container.

The two alternative processes (Process 1 and Process 2) can be more easily understood if the processes are considered to take place stepwise as follows:

PROCESS 1

Process 1 assumes that the expanding vapor phase of the aerosol container mixes completely with the air in the gage. The final composition of the vapor phase of the container is the same as that in the gage.

*Step 1*

When the valve between the container and the gage is opened, the vapor phase of the aerosol expands into the gage until the pressure in the aerosol and the gage are about equal. During this expansion, the vapor phase of the aerosol and the air in the gage are assumed to mix completely.

*Step 2*

Sufficient liquid vaporizes from the surface of the liquefied propellant to maintain the pressure exerted by the propellant at a relatively constant value.

The volume of the vapor phase of the aerosol can now be considered to consist of the original vapor phase in the container plus the volume of the gage. On the basis of the original assumption that the air concentration in the aerosol container initially was greater than that in the gage and that the volume of the gage was less than that of the vapor phase, the final concentration of air in the combined volumes of the vapor phase of the initial aerosol and the gage will be less than that originally present in the aerosol container. Therefore, after expansion into the gage, the pressure due to air will be less than that originally present in the container and the pressure recorded on the gage will be less by this factor than the original pressure in the aerosol container.

*Step 3*

The container and gage are now shaken to reestablish equilibrium between the air in the liquid phase and that in the vapor phase. When this occurs, the pressure will rise for the following reason: the distribution of air between the liquid and vapor phases of an aerosol is a function of the volume ratio of the liquid phase to the vapor phase (Ref. 2). Since the vapor phase of the aerosol after expansion into the gage can now be considered to be increased by that of the gage, the distribution ratio will change and air will leave the liquid phase in order to establish equilibrium at the new liquid phase/vapor phase ratio. The increased concentration of air in the vapor phase will cause the pressure to rise.

Therefore, if Process 1 takes place, the pressure will first decrease as a result of expansion into the gage and this will be followed by an increase in pressure after the container and gage are shaken.

PROCESS 2

The vapor phase of the aerosol during expansion does not mix with the air in the gage. The air in the gage, therefore, merely acts as a piston for transmittal of pressure to the gage. If this process takes place, the following steps can be considered to take place during the pressure measurement:

*Step 1*

When the valve between the can and the gage is opened, the vapor phase of the aerosol expands into the gage until the pressure of the expanded vapor phase and the pressure in the gage are equal.

*Step 2*

Sufficient liquid vaporizes from the liquefied propellant to maintain a constant propellant pressure in the vapor phase.

*Step 3*

The container is now shaken. Some of the air originally present in the aerosol was lost by expansion into the gage. Therefore, some air will have to leave the liquid phase and enter the vapor phase in order to maintain the original distribution ratio of air between the two phases. In this case, the ratio of the volume of the liquid phase and the vapor phase is the same as that initially present in the container, since the redistribution of air occurs only in the aerosol container.

*Step 4*

The redistribution of air in the vapor phase that results from shaking increases the concentration of air in the vapor phase and consequently the pressure increases. Since the pressure in the aerosol is now higher than that in the gage, the vapor phase of the aerosol will again expand into the gage until the pressures in the system equalize.

The second expansion of the vapor phase of the aerosol into the gage causes a further loss of air from the aerosol and a second redistribution of air between the liquid and vapor phases occurs upon shaking. This causes another increase in pressure in the aerosol and another expansion into the gage. Therefore, the cycle continues until equilibrium is eventually established.

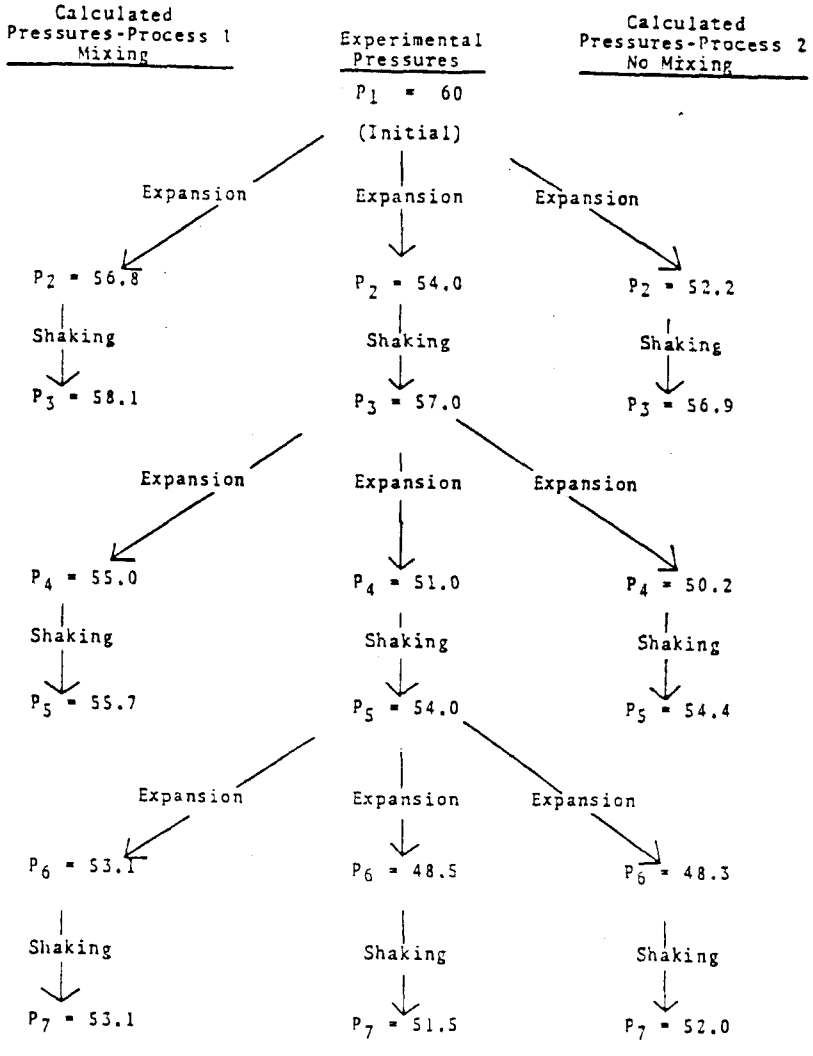
The overall result if Process 2 takes place is an initial decrease in pressure as the vapor phase expands into the gage, followed by a higher pressure when the container and gage are shaken. The pressure continues to increase gradually until equilibrium is established. These results are similar to the results of Process 1, but the magnitude of the changes is considerably different than those from Process 1.

A comparison of the pressures calculated for Process 1 and Process 2 with the experimentally measured pressures in Table I indicates that Process 2 is the predominant process that occurs when the vapor phase of an aerosol expands into the gage. In most cases, the calculated pressures of Process 2 are fairly close to the experimentally measured pressures. There is a slight tendency for the measured pressures to fall in between the pressures calculated for Process 1 and those calculated for Process 2. This probably indicates that there is a slight mixing of the expanding vapor phase of the aerosol with the air in the gage at the aerosol vapor phase-air boundary. Although the air in the gage acts as a piston for transmittal of pressure, the interface between the air in the gage and the expanding vapor phase of the aerosol is somewhat diffuse, as would be expected. In general, however, there is very little mixing of the expanding vapor phase of the aerosol with the air in the gage.

The fact that the expanding vapor phase of the aerosol did not mix significantly with the air in the gage confirms previous evidence for this behavior reported by H. M. Parmelee

TABLE I

Comparison of Experimental Pressures With Calculated Pressures (psig at 70°F)




(Reference 4). Parmelee noted that when air was pumped into a cylinder of "Freon-12", the air acted initially as a piston and compressed the "Freon-12", vapor. Under static conditions, three hours were required for the air to mix with the "Freon-12" vapor.

Since Process 2 is the predominant process that occurs, the pressure will always decrease when the vapor phase of the aerosol expands into the gage if air is present in the vapor phase. The decrease in pressure will result from the change in air pressure in the aerosol as the air pressure drops during the expansion into the gage.

It is interesting to speculate what would happen to the pressures if Process 1 occurred with an aerosol product containing no air in the vapor phase when pressures were taken with a gage filled with air at atmospheric pressure. In this case, if the expanding vapor phase of the aerosol mixed with the air in the gage, the final vapor phase, which would consist of that of the aerosol and the gage, would contain more air than was initially present in the vapor phase of the aerosol alone. The pressure after expansion into the gage would be higher than the initial pressure in the aerosol as a result of the added pressure of the air. Upon shaking, some air would dissolve in the liquid phase of the aerosol in order to establish equilibrium and this would decrease the concentration of air in the vapor phase. Therefore, the pressure would decrease upon shaking, but still would be higher than the original pressure in the aerosol.

### *Experimental*

As previously mentioned, the pressures from both Process 1 and Process 2 were calculated. The equations that were developed for the calculations and examples of the calculations are covered in the appendix. A comparison of the experimentally determined pressures with the calculated pressures indicated that Process 2 was the predominant process occurring during expansion of the vapor phase of the aerosol into a gage at a lower pressure.

The experimental tests were carried out as follows: an empty 6-ounce aerosol container was capped with a valve without a dip tube and thus was filled with air at atmospheric pressure. The container was pressure loaded to 84.5% volume fill with an accurately prepared mixture of "Freon-12"/"Freon-11" (50/50). The vapor phase in the aerosol after the addition of the propellant was 35 cc.

Pressures were determined using a calibrated Ashcroft gage with 2-lb. scale division. Pressures were estimated to the nearest 0.5 psi. The gage was connected to the aerosol container by means of a can puncturing device equipped with valves for prepressuring the gage and allowing the gage to return to atmospheric pressure. The total volume of the gage and connections was 24 cc. The aerosol container was thermostated at a temperature of 70°F.

The initial pressure in the aerosol container ($P_1$) was determined with a prepressurized gage and found to be 60.0 psig at 70°F. The pressure of the propellant at 70°F. was 37.5 psig (Reference 3) and the pressure due to air therefore was 22.5 psi. After the pressure had been measured, the valve between the gage and the aerosol container was closed and the gage was vented and returned to atmospheric pressure. The valve between the gage and the aerosol container was then opened and the vapor phase of the aerosol was allowed to expand into the gage. Care was taken not to shake the aerosol container during the expansion into the gage. The pressure after expansion was 54.0 psig ($P_2$). The aerosol container was then shaken to reestablish

equilibrium for the air between the liquid phase and vapor phase. The pressure rose to 57.0 psig ($P_2$) and then remained essentially constant. The valve between the gage and the aerosol container was closed and the gage was again vented and returned to atmospheric pressure. The cycle of allowing the aerosol to expand into the gage at atmospheric pressure without shaking, followed by shaking to establish equilibrium, was repeated two more times.

The experimentally determined pressures for the three cycles are given in Table I along with the pressures that were calculated for both Process 1 and Process 2. For both processes, the pressures after expansion into the gage were calculated from the experimentally determined pressures $P_1$, $P_3$ and $P_5$. However, the pressures for Process 1 and Process 2 after shaking were calculated from the previously calculated pressures after expansion. This is illustrated diagrammatically in Table I.

I. *Calculations of Pressures Assuming Complete Mixing of the Vapor Phase of the Aerosol with the Air in the Gage*

A. *Pressure After Expansion into the Gage*

The initial pressure in the aerosol ($P_1$) was 60.0 psig at 70°F. The pressure of the propellant, "Freon-12/"Freon-11" (50/50) was 37.5 psig, as reported in Reference 3. Subtraction of the propellant pressure from the total pressure gave the initial air pressure of 22.5 psi.

The mols of air in the vapor phase of the aerosol were calculated using the relationship

$$n \text{ (mols air)} = \frac{PV}{RT} = \frac{\frac{22.5}{14.7} \times 35}{82.06 \times 294.1} = 0.00222$$

The total mols of air in the aerosol container were calculated from the distribution ratio of air in the aerosol and the number of mols of air in the vapor phase. The distribution ratio of air at 84.5% volume fill is 74% in the liquid phase and 26% in the vapor phase (Reference 2). The total mols of air in the aerosol container therefore were

$$\frac{0.00222}{0.26} = 0.00853$$

The mols of air in the gage were calculated from the volume of the gage, 24 cc, assuming the air in the gage at atmospheric pressure.

$$n \text{ (mols air in gage)} = \frac{1 \times 24}{82.06 \times 294.1} = 0.00098$$

After expansion into the gage and mixing, the total volume of the vapor phase is 35 + 24 = 59 cc. The total number of mols of air in the new vapor phase is equal to 0.00222 + 0.00098 = 0.0032. The pressure of the air in the expanded vapor phase is

$$P \text{ (air)} = \frac{0.0032 \times 82.06 \times 294.1}{59} =$$

1.31 atm = 19.3 psi

The total pressure in the aerosol and gage therefore is 37.5 + 19.3 = 56.8 psig.

B. *Pressure After Shaking*

Considering that the gage is now part of the aerosol, the new volume of the aerosol is 225 cc + 24 cc = 249 cc. The percent liquid fill therefore has changed from 84.5% to 76.4%. The distribution ratio of air therefore changes from 74% in the liquid phase and 26% in the vapor phase to 64% in the liquid phase and 36% in the vapor phase.

The total mols of air in both the aerosol container and gage is 0.00853 + 0.00098 = 0.00951. The number of mols of air in the vapor phase, after shaking and redistribution of the air, is 0.36 × 0.00951 = 0.00342. The pressure of the air after shaking therefore is:

$$P \text{ (air)} = \frac{0.00342 \times 82.06 \times 294.1}{59} =$$

1.40 atm or 20.6 psi

The total pressure in the aerosol and gage is 37.5 + 20.6 = 58.1 psig.

The pressures for the two following cycles of expansion and shaking were calculated in a similar manner.

II. *Calculations of Pressures Assuming no Mixing of the Vapor Phase of the Aerosol with the Air in the Gage*

In this case it is assumed that the expanding vapor phase of the aerosol merely compresses the air in the gage and does not mix with it.

The decrease in pressure results from the change in air pressure during the expansion. In order to calculate the pressures for Process 2, it was necessary to derive an equation which gives the increase in volume of the vapor phase after expansion. The following assumptions were made in the derivation:

1. The expansion of the vapor phase is isothermal;
2. The pressure of the formulation due to propellant remains constant as a result of further vaporization of the liquid phase during the expansion;
3. No mixing of the expanding vapor phase with the air in the gage occurs.

Actually, two equations were derived. The first equation is cumbersome and was not used in the present calculations. The terms used in the derivation and their meanings are as follows.

$P_i$ = Initial pressure in the container
$P$ = Final pressure in either container or gage
$P_p$ = Pressure of propellant
$P_a$ = Initial pressure of air in container
$P_{fa}$ = Final pressure of air in container
$V$ = Volume of vapor phase in container
$V_g$ = Volume of gage
$P_g$ = Initial pressure in gage
$P_{fg}$ = Final pressure in gage
$X$ = Increase in volume of vapor phase of aerosol during expansion

The derivation of the first equation was as follows:

(1) $P = P_p + P_{fa} = P_{fg}$

(2) $P_a V = P_{fa} (V + X)$

(3) $P_{fa} = \frac{P_a V}{V + X}$

(4) $P_g V_g = P_{fg} (V_g - X)$

(5) $P_{fg} = \frac{P_g V_g}{V_g - X}$

(6) $P = P_p + \frac{P_a V}{V + X} = \frac{P_g V_g}{V_g - X}$

(7) $P_p + \frac{P_a V}{V + X} = \frac{P_g V_g}{V_g - X}$

Solving the equation for X leads to the following quadratic equation. The intermediate steps in the solution are available if desired.

(8)

$$X = -\left[V_g\ (P_g - P_p) + P_1 V\right] + \sqrt{\left[V_g\ (P_g - P_p) + P_1 V\right]^2 - 4P_p\left[V\ V_g\ (P_g - P_1)\right]} \Big/ 2\ P_p$$

Equation 8 is obviously cumbersome to use. Therefore, a new equation was developed in which a trial value for X is improved by iteration. This is a standard procedure used in mathematics.

The new equation was developed from equation 7 by substituting $X_o$ for X on the left hand side of the equation as follows:

(9)
$$P_p + \frac{P_a V}{V + X_o} = \frac{P_g V_g}{V_g - X}$$

Solving equation 9 for X leads to the final equation as follows:

(10)
$$X = V_g\left[1 - \frac{P_g}{P_p + P_a\left(\frac{V}{V + X_o}\right)}\right]$$

In using equation 10, values of X are assumed and substituted for $X_o$. The equation is then solved for X. The value of X thus obtained is then substituted for $X_o$ and the equation again solved for X.

After X has been obtained, the final pressure in the vapor phase due to air is obtained from the equation.

$$P_{fa} = \frac{P_a V}{V + X}$$

A. *Pressure After Expansion into the Gage*

In order to calculate the pressure after expansion, it was first necessary to determine X, the increase in volume, using equation 10. The following values were used for equation 10:

$P_o = 52.2$ psia at 70°F
$P_g = 14.7$ psia
$P_a = 22.5$ psia
$V = 35$ cc
$V_g = 24$ cc

A trial value of 18 cc was first assumed for X and substituted in equation 10 for $X_o$ as follows:

$$X = 24\left[1 - \frac{14.7}{52.2 + 22.5\left(\frac{35}{35 + 18}\right)}\right]$$

Solving the equation for X gave a value of 18.7 cc. This value was then substituted for $X_o$ and the equation again solved for X. The value of X remained at 18.7 cc and further substitution was not necessary. The air pressure after expansion was then calculated as follows:

$$P_{fa} = \frac{35}{35 + 18.7} \times 22.5 = 14.7 \text{ psi}$$

The total pressure in the aerosol then is 37.5 + 14.7 = 52.2 psig at 70°F.

B. *Pressure After Shaking*

Before expansion into the gage, there were 0.00222 mols air vapor phase, and 0.00631 mols air liquid phase, for a total of 0.00853 mols air in the aerosol container. After expansion, the number of mols air remaining in the vapor phase of the aerosol container was 35/53.7 x 0.00222 = 0.00145 mols. The total mols of air in the aerosol container after expansion therefore was 0.00631 + 0.00145 = 0.00776.

The distribution ratio of air in the aerosol container is 74% liquid phase and 26% vapor phase. Therefore, assuming that the redistribution of air occurs only in the aerosol container upon shaking, the number of mols of air in the vapor phase after shaking is 0.26 x 0.00776 = 0.00202.

The pressure of air in the vapor phase then is:

$$P\ (\text{air}) = \frac{0.00202 \times 82.06 \times 294.1}{35} =$$

1.39 atm = 20.4 psi

The total pressure in the aerosol is 37.5 psig + 20.4 psi = 57.9 psig at 70°F. However, the pressure in the aerosol is now higher than that in the gage, so a second expansion into the gage occurs and it is necessary to obtain a second value for X. Assuming an initial value of 6 cc for X and substituting for $X_o$ in equation 10 gives a value of 1 cc. After several more trial substitutions, a final value of 1.7 cc for X was obtained. The final pressure of the air after the expansion therefore is 20.4 x 35/36.7 = 19.4 psi.

The total pressure in the aerosol after shaking therefore is:

P = 37.5 + 19.4 = 56.9 psig at 70°F.

The pressures after expansion into the gage and subsequent shaking for the next two cycles were calculated similarly.

## Summary

The expansion of the vapor phase of an aerosol product containing air into a gage at a lower pressure can occur by two different processes. Either the vapor phase of the aerosol can mix completely with the air in the gage or the air in the gage can act merely as a piston for transmittal of pressure to the gage. In the latter case the vapor phase of the aerosol does not mix with the air in the gage. Comparison of pressures calculated for the two different processes with experimentally determined values shows that essentially no mixing of the vapor phase of the aerosol with the air in the gage occurs.

The derivation of equations used to calculate the pressures, assuming no mixing of the vapor phase of the aerosol with the air in the gage, is shown.

## References

1. "Freon" Aerosol Report, FA-11, "A Method for Measuring the Vapor Pressure of Aerosol Products."
2. "Freon" Aerosol Report, FA-15, "The Effect of Air on Pressure In Aerosol Containers."
3. "Freon" Aerosol Report, FA-22, "Vapor Pressure and Liquid Density of 'Freon' Propellants."
4. Parmelee, H. M., 'Solubility of Air in 'Freon-12' and 'Freon-22'," Refrigerating Engineering, June 1951.

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