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ERRATA

Page 22, mid-page, correct the following code:

Old code: $A = 6.4837D0$

Corrected code: $A = 6.4827D0$

Page 22, near the bottom of the page, correct the following code:

Old code: $A = 2.085371D1$

Corrected code: $A = 2.08537D1$

Page 23, Line 12, correct the following code:

Old code: $K = (C+D*RDEN) / 553.0D0 * 1.0D5$

Corrected code: $K = (C+D*RDEN) / 543.0D0 * 1.0D5$

Manual of Petroleum Measurement Standards Chapter 11—Physical Properties Data

Addendum to Section 2, Part 2—Compressibility Factors for Hydrocarbons, Correlation of Vapor Pressure for Commercial Natural Gas Liquids

FIRST EDITION, DECEMBER 1994

American Petroleum Institute
1220 L Street, Northwest
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Measurement Coordination

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FOREWORD

A simplified correlation for the equilibrium bubble point pressure, vapor pressure, of commercial natural gas liquids, NGLs, has been developed. This correlation was developed in response to the industry's need for a simplified correlation to be used when adjusting densities from flowing conditions to a set of standard conditions. Methods for improving the accuracy and extending the correlation are also discussed.

The purpose of this procedure is to provide a simplified means of estimating flowing equilibrium vapor pressures of various Natural Gas Liquids, using relative density (60°F/60°F) and flowing temperature inputs. This procedure is proposed for use on GPA Standard Specification 2140, commercial HD-5 Propane, Iso-Butane, Normal Butane, and 12-14 psia Natural Gasoline between -50°F and +140°F. The intended application of this procedure is for determining the value of P_e (equilibrium vapor pressure at flowing conditions) required for determining pressure volume correction factors as specified in API MPMS Chapter 11.2.1 and 11.2.2.

Three primary correlations (commercial HD-5 Propane, Butanes, and Natural Gasoline mixtures) were developed from data. To provide continuity, two secondary correlations or extrapolations were derived which connect or bridge the three primary correlations.

Minor variations from the predicted vapor pressure to actual are to be expected in the primary equation due to the possible combinations of product compositions which may result in the same relative density product. The magnitude of these variations, however, is expected to have minimal overall impact on the volume correction factors determined from its use.

Due to the unconstrained range of compositions possible in non-specification mixtures, greater variations may occur between an actual sample and the correlation values in the extrapolated regions, and accuracy should be checked by the user.

These bridge correlations may be utilized for settlement purposes if agreed to between the contracting parties. However, additional accuracy may be obtained by developing a modified correlation as indicated in the procedure, based upon test data.

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Suggested revisions are invited and should be submitted to Measurement Coordination, Exploration and Production Department, American Petroleum Institute, 1220 L Street, N.W., Washington, D.C. 20005.

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Chapter 11—Physical Properties Data

ADDENDUM TO SECTION 2, PART 2—COMPRESSIBILITY FACTORS FOR HYDROCARBONS, CORRELATION OF VAPOR PRESSURE FOR COMMERCIAL NATURAL GAS LIQUIDS

1 Background

In custody transfer applications there is a need to convert flowing volumes of liquids to equivalent volumes of liquid at some set of standard conditions, usually 60°F and the greater of one atmosphere pressure or the equilibrium vapor pressure of the liquid. The techniques for converting densities from flowing conditions to standard conditions generally are of the form:

$$\rho_{60} = F_t \times F_p \times \rho$$

Where:

ρ_{60} = Density at 60°F and the greater of one atmosphere pressure or the equilibrium vapor pressure of the liquid.

ρ = Density at flowing conditions.

F_t = Correction factor for temperature effects.

F_p = Correction factor for pressure effects.

Two methods used for calculation of the F_p term are standardized by the American Petroleum Institute (1984 and 1986). These methods require the equilibrium bubble point pressure (P_e), the vapor pressure, at the flowing conditions in order to calculate the correction factor. Although the vapor pressure of the flowing liquid could be measured, it generally is not. The vapor pressure can be calculated from compositional information to the required accuracy using one of several techniques, but the composition is not always measured for natural gas liquids, NGLs. Therefore, a correlation for the vapor pressure of NGLs based upon normally measured properties was desired.

A correlation for the vapor pressure of NGLs was the correlation developed by Hillburn (1968) (see Figure 1) which requires only the vapor pressure at 100°F. This correlation was primarily developed for use with commercial propanes, but it has been applied to other NGLs. A major limitation of this correlation is the fact that it can predict negative absolute vapor pressure. Another limitation is that it requires the 100°F vapor pressure value. This value is often measured to meet transportation regulation requirements, but it is not always measured. The correlation seems to work fairly well for propane mixtures, but does not work at all well for natural gasolines.

The problems and limitations of the Hillburn correlation prompted this project to develop an alternative correlation based only upon the relative density, a value that is always measured. A less empirical correlation form was also desired.

Since the vapor pressure curve for a mixture has a shape very similar to a pure component vapor pressure curve at low to moderate pressures, it was decided to build the correlation around one of the simplest pure component vapor pressure models that could reproduce experimental vapor pressure data reasonably well. Of the several models reviewed, the simple Antoine (Reid, et al. 1987) vapor pressure model was chosen. It was found that a fairly good correlation of the Antoine constants in terms of relative density was possible, yielding the final correlation form shown in Figure 2. Table 1 lists the constants required for the correlation in each of its applicable ranges. Figure 3 is a plot of the vapor pressures that would be predicted by the new correlation at several key temperatures in the temperature range of the correlation.

2 Correlation Development

2.1 PROPANES

2.1.1 Product Specifications

For the purpose of correlation development, product specifications from GPA Standard 2140-88, "Liquefied Petroleum Product Gas Specifications and Test Methods," given in Table 2, were used. Although the presence of olefins is allowed by the specifications, it was assumed that no olefins were present since they generally have a much higher market value and would be preferentially recovered. During the course of the correlation development, it became

$$P = P_{100} + Q \times (P_{100} + 20) \times \tan(\alpha)$$

For $t < 100^\circ\text{F}$

$$Q = -1.0$$

$$\alpha = 0.017454 \times (36.95865 - 0.1363394 \times t - 0.000927206 \times t^2 - 0.00001409909 \times t^3)$$

For $t \geq 100^\circ\text{F}$

$$Q = 1.0$$

$$\alpha = 0.0143464 \times (t - 100)$$

Where:

P = Vapor pressure at t (psig).

t = Temperature ($^\circ\text{F}$).

P_{100} = Vapor pressure at 100°F (psig).

Figure 1—Old Correlation for Vapor Pressures (Hillburn, 1968)

Table 1—Constants for New Correlation

Applicable Range	A ₀	A ₁	B ₀	B ₁
0.490 ≤ G ≤ 0.510	-6.4747 ±0.7023	37.083 ±1.405	12038.0 ±335.5	-31296.5 ±671.0
0.510 < G < 0.560	11.5454 ±1.1657	1.7490 ±1.164	1378.8 ±360.9	-10396.1 ±555.9
0.560 ≤ G ≤ 0.585	6.4827 ±0.4220	10.790 ±0.735	3721.5 ±201.6	-14579.5 ±351.3
0.585 < G < 0.625	6.5412 ±3.1017	10.690 ±5.201	6514.5 ±518.1	-19353.9 ±736.3
0.625 ≤ G ≤ 0.676	20.8537 ±3.7280	-12.210 ±5.722	-6765.6 ±489.0	1894.3 ±750.6

Note: Constants are in U.S. engineering units for new vapor pressure correlation for each relative density range. Constants are given to more digits than are significant in order to allow reproduction of results. The confidence limits given are 90 percent confidence limits.

apparent that a propane mix having a relative density of 0.490 or 0.495 could not meet these specifications. This fact was later proven by experimental measurements (Parrish, 1987). Since several member companies wanted the correlation to apply to propane mixes having relative densities of 0.490 and 0.495, it was agreed that for these cases the 100°F vapor pressure specification would be relaxed in order to obtain the desired relative density.

2.1.2 Data Collection

As part of the correlation project definition, it was agreed that the vapor pressure data would be generated from the Soave-Redlich-Kwong (SRK) equation of state (Soave, 1972) and that densities would be generated from the COSTALD correlation (Hankinson, et al., 1979 and Thomson, et al., 1982) using parameters from the Phillips Thermo-physical Data System (Embry, 1985). It was found that it was necessary to modify the values of the acentric factor used with the SRK in order to match the 100°F vapor pressures to the desired accuracy. The values of the pure component parameters used are listed in Table 3. Volume percent compositions were converted to molar compositions using the ρ_{60} values. The binary interaction parameters needed for the SRK are shown in Table 4.

The COSTALD correlation has been shown by Thomson, et al. (1982), to give accurate NGL densities, on the order of ±0.2 percent. A specially modified version of the correlation has been developed for LNGs (Hankinson, et al., 1982), but was not applicable to this work.

The compositions of several propane samples which met the product specifications at relative densities of 0.490, 0.495, 0.500, 0.505, and 0.510 were calculated through the process of trial and error. It was found that there was enough leeway in the specifications that it was possible to generate more than one composition that would meet them at each relative density. Only the compositions which yielded the highest and lowest 100°F vapor pressure, shown in Table 5,

were retained for further analysis. The variation between the high and low vapor pressure cases for relative densities of 0.500 and 0.510 was negligible. Therefore, only one case was retained for these two relative densities.

Vapor pressure data was generated for each case over the entire temperature range of -50°F to 140°F in 10°F increments using the SRK. This provided twenty vapor pressure points for each case, for a total of 160 points.

2.1.3 Data Regression

For the purpose of data regression it was decided that a single set of vapor pressure data would be used at each relative density. The "representative" vapor pressure used for samples which had both an upper and a lower vapor pressure was chosen such that it would yield an equal percentage error from each of the true vapor pressures. This choice of the "representative" pressure is almost the same as would be chosen by the regression. The "representative" pressure is calculated as the harmonic average of the high and the low vapor pressures. Only the "representative" vapor pressure data were used in the data regression.

Regression of the generated vapor pressure data was performed in three steps:

- Regression of each sample individually to the equation:
 $\ln(P) = A + B / (t + C)$.
- Regression of A and B as linear functions of relative density.
- Regression of all samples simultaneously to the correlation equation.

By performing the data regression in three steps, a check of the appropriateness of the chosen functional forms and a

$$\ln(P) = (A_0 + A_1 \times G) + (B_0 + B_1 \times G) / (t + C)$$

Where:

- P = Vapor pressure at t (psia).
- t = Temperature (°F).
- G = Relative density (60°F/60°F)^a.
- C = A constant. For all ranges C = 443.0°F.
- A₀ = Values for different correlation ranges are given in Table 1. Units are Ln (psia).
- A₁ = Values for different correlation ranges are given in Table 1. Units are Ln (psia).
- B₀ = Values for different correlation ranges are given in Table 1. Units are Ln (psia)/°F.
- B₁ = Values for different correlation ranges are given in Table 1. Units are Ln (psia)/°F.

Note: The correlation is limited to -50°F ≤ t ≤ 140°F, and 0.490 ≤ G ≤ 0.676.

^a It is assumed that an accurate value of the relative density will be used with this correlation. The interested reader should refer to the applicable ASTM standards for reliable measurement methods.

Figure 2—New Correlation for Vapor Pressures

check of the effects of each regression assumption of the goodness of fit could be performed.

Regression of the samples individually yielded fits of the data having a maximum error of 1.0 percent and an average absolute error of 0.3 percent over the entire temperature range. A residual plot did not show any significant systematic variations, so the correlation form was accepted without any further investigation.

At this point, several different values of *C* were tried to see if the maximum and average errors could be reduced. There was no significant reduction of error possible, so the value of *C* was “frozen” at the reported value of 443°F for all further regression analyses.

Plots of the *A* and *B* values determined by the individual regressions as functions of relative density showed an almost linear dependence. Residual plots from the linear regressions of the *A* and *B* values showed some systematic variation, but addition of higher order relative density terms neither improved the fit nor removed the systematic deviations. Therefore, the linear dependence was chosen.

The previous sets of analyses yielded the correlation form given in Figure 2 which was then used for regression of all the propane data. For the data included in the analysis, the maximum error was 3.9 percent and the average absolute error was 0.8 percent. When checked against all of the data rather than just the “representative” data, the correlation had the maximum error of 7.8 percent, an average absolute error of 1.8 percent and a bias of –0.2 percent. The ability of the correlation to reproduce the raw propanes data at –50°F, 0°F, 60°F, 100°F, and 140°F is shown in Figure 4, Figure 5, Figure 6, Figure 7, and Figure 8 respectively.

2.1.4 Correlation Comparison

Comparison of the new correlation to the Hillburn correlation for the propanes shows that the new correlation is superior. Table 6 gives a summary comparison of the new correlation and the old Hillburn correlation at selected points for each of the samples. At most temperatures the new correlation is superior.

Table 2—Liquefied Petroleum Gas Specifications (GPA Standard 2140-88)

Product Characteristics	Commercial Propane	Commercial Butane	Commercial B-P Mixtures	Propane HD-5	Test Method
Composition	Predominantly propane and/or propylene	Predominantly butanes and/or butylenes	Predominantly mixtures of butanes and/or butylenes with propane and/or propylene	Not less than 90 liquid volume percent propane; not more than five liquid volume percent propylene	ASTM D-2163-82
Vapor pressure at 100°F, psig, maximum	208	70	208	208	ASTM D-1267-84
Temperature at 95 percent evaporation, °F maximum	–37	36	36	–37	ASTM D-1837-86
Butane or heavier, liquid volume percent, maximum	2.5	–	–	2.5	ASTM D-2163-82
Pentane or heavier, liquid volume percent, maximum	–	2.0	2.0	–	ASTM D-2163-82
Residue on evaporation of 100 milliliters, maximum	0.05 ml	–	–	0.05 ml	ASTM D-2158-85
Oil stain observation	Pass ^a	–	–	Pass ^a	ASTM D-2158-85
Corrosion, copper strip, maximum	No. 1	No. 1	No. 1	No. 1	ASTM D-1838-84
Total sulfur, ppmw	185	140	140	123	ASTM D-2784-80
Moisture content	Pass	–	–	Pass	GPA Propane Dryness Test (Cobalt Bromide) or D-2713-86
Free water content	–	None	–	None	–

^a An acceptable product shall not yield a persistent oil ring when 0.3 milliliters of solvent residue mixture is added to a filter paper in 0.1 increments and examined in daylight after two minutes as described in ASTM D-2158.