

# Determining Hydrocarbon Dew Point per Gas Chromatographic Analysis and Equations of State

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## Introduction

The determination of the *hydrocarbon dew point* (HDP) for natural gas has recently become a critical issue for the natural gas industry because of the rapid expansion of interconnecting pipelines and the rise of the liquefied natural gas (LNG) as an international source of natural gas. Whereas previously the gas in a pipeline would come from a small number of known producers, the gas flowing through the pipeline today could have come from many varied sources including traditional gas plant producers (de-hydration, CO<sub>2</sub>, H<sub>2</sub>S and N<sub>2</sub> control and removal of condensates), coal bed methane producers (98% methane), low cost producers (de-hydration only) or global exporters of LNG.

Economic factors have also played a role in the changing quality of the gas. Unfavorable natural gas/NGL product price spread historically have resulted in HDP concerns for pipeline operators as producers who previously have stripped the heavier components out of the gas to produce condensates have realized a greater return by leaving the higher energy value heavy components in the export natural gas.

High HDP natural gas becomes an issue to the transporters and the end-users of the gas when the heavier components start to “drop-out” into the liquid phase as the temperature of the gas drops below the HDP. Hydrocarbon liquids in the gas stream can cause hydrate formation, increased compression costs, issues with pressure regulator stations in which the latent heat of vaporization (the large temperature drop because of the vaporization of the liquid components) can cause freezing of the valves, and damage to end-user equipment such as gas turbines.

To protect against this risk, transporters are beginning to mandate to the suppliers of the gas limits for the HDP, which in turn requires a reliable method of reporting the HDP at the receipt point. The HDP value is used for the protection of pipelines and end users, so it is important that a conservative approach should be taken in the measurement and use of the HDP value.

Two methods for determining HDP are currently in widespread use:

**Dew-Scope** – A mirror is chilled and as the dew point of the gas is reached a hydrocarbon mist is formed on the mirror. A light reflected on the mirror is obscured by the mist, thus inferring the temperature of the dew point at the pressure of the test. As a certain amount of mist (liquid drop-out) must be formed before the trigger of the detection circuit, the results will generally be lower than the actual dew point.

**Calculation using an Equation of State** – By entering the composition of the natural gas into a recognized equation of state, the theoretical HDP can be calculated for any pressure as well as the *cricondentherm* (the highest dew point temperature at any pressure). The validity of the calculated value depends on the accuracy of the composition used especially for the higher carbon number hydrocarbons (C<sub>6</sub> to C<sub>9</sub>).

A *gas chromatograph* (GC) is already in use at most custody transfer location to measure the composition and calculate the physical properties of the gas, such as energy value (BTU or MJ), specific gravity and compressibility. To incorporate the functionality to calculate the HDP is simply an extension of the capabilities of the GC. This paper shall describe the requirements of a GC to perform this calculation, and a method employed by one GC manufacturer.

## Equations of State

Firstly we shall look at the two most commonly used equations of state used in the natural gas industry and how they are used.

The two most commonly used and accepted equations of state are:

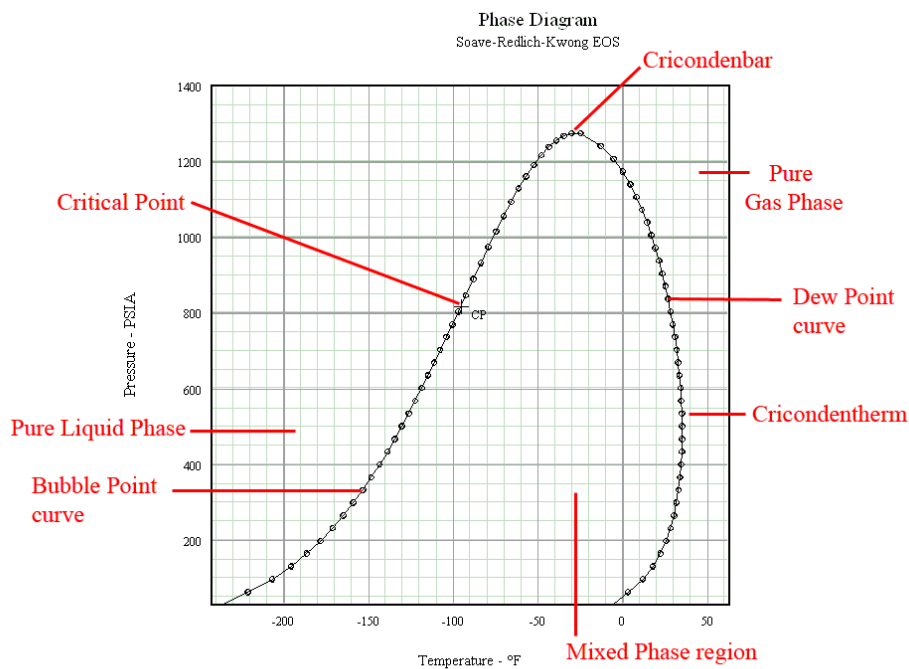
Peng-Robinson (PR) (1976) equation of state<sup>1</sup>: This is the most commonly used method for “pipeline quality gas.”

Redlich-Kwong-Soave (RKS) (1972) equation of state: An improvement by Soave on the original Redlich-Kwong (1949) equation of state.

The results from each of the two equations of state generally agree to within 4 DegF (2 DegC) and selecting which method to use is dependent on the application. The RKS method will generally yield a higher dew point result and the PR equation has been generally adopted by the natural gas industry as the most common method.

The method of representing the results of the equations of state is the *phase diagram*. This produces a graphical representation of the expected physical state of the mixture for the range of Pressures and Temperatures.

Figure 1 - Typical Phase Diagram



At this stage it is important to define some of the terms used when discussing HDP, and where they are represented on a phase diagram.

- **Dew Point** – The temperature at which components of a gas mixture will start to change from the gas phase to the liquid phase, or “drop out,” at a **nominated pressure**. Whenever a dew point is reported, the pressure at which it is calculated should also be stated.
- **Cricodentherm** – The highest dew point temperature, at any pressure. Often this is written in gas quality documents as the “highest dew point at any pressure.”
- **Cricodenbar** – The highest pressure at which two phases can exist.

1. <sup>1</sup> Peng, DY, and Robinson, DB. *A New Two-Constant Equation of State*. Industrial and Engineering Chemistry: Fundamentals. Vol. 15 (1976) pp. 59-64.

- **Critical point** – The pressure and temperature at which distinct liquid or gas phases ceases to exist.

### **GC Requirements**

As the HDP is the condition when the heavy components begin to drop out into the liquid phase, the accurate measurement of the heavier components is critical for a meaningful determination of the HDP. The most common method for determining the composition of the pipeline gas for custody metering is by using a GC, typically of a “C6+” analysis. This will measure nitrogen, carbon-dioxide, the individual hydrocarbons from methane up to normal-pentane, and report the heavier components as a combined C6+ measurement.

For energy calculation, the C6+ component is split into a fixed ratio of n-hexane, n-heptane and n-octane (refer Table 1.) As “pipeline quality gas” has a relatively small concentration of C6+, this assumption will provide a very small error for the energy value and is usually well within the uncertainty of the entire analyzer system.

**Table 1 - Common C6+ Composition Splits**

	<b>47/35/17</b>	<b>GPA 2261</b>	<b>50/50/0</b>	<b>58/28/14</b>
n-Hexane	47.466	60	50	57.143
n-Heptane	35.340	30	50	28.572
n-Octane	17.194	10	0	14.285

However, using a fixed ratio for the HDP can result in very large errors as it is the heavy components that will fall out as a hydrocarbon liquid, and relatively small changes in the concentrations of C6’s, C7’s, C8’s and C9+ components will affect the HDP considerably. As discussed in the introduction, natural gas supplies for a particular delivery point can come from many different producers that may process the gas to different degrees using different processes. The result is that a fixed ratio of the higher components will not hold true for all

**Table 2 - C6+ and C9+ Measurement Ranges**

<b>Component</b>	<b>Standard C6+ Measurement Range</b>	<b>C9+ Measurement Range</b>
Methane	65 to 100%	65 to 100%
Ethane	0 – 20%	0 – 20%
Propane	0 – 10%	0 – 10%
n-Butane	0 – 5%	0 – 5%
Iso-Butane	0 – 5%	0 – 5%
n-Pentane	0 – 1%	0 – 1%
Iso-Pentane	0 – 1%	0 – 1%
Neo-Pentane	0 – 1%	0 – 1%
C6+	0 – 0.7%	-
Nitrogen	0 – 20%	0 – 20%
Carbon Dioxide	0 – 20%	0 – 20%
Hexanes	-	0 – 1%
Heptanes	-	0 – 1%
Octanes	-	0 – 0.5%
C9+	-	0 – 0.5%

variations of the natural gas in a pipeline, and will not be representative of the measured gas. This is critical in the HDP calculation in which the larger components have a much greater affect on the results than the C1 to C5 components.

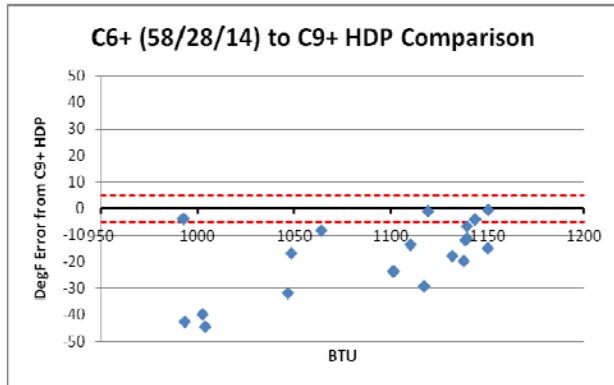
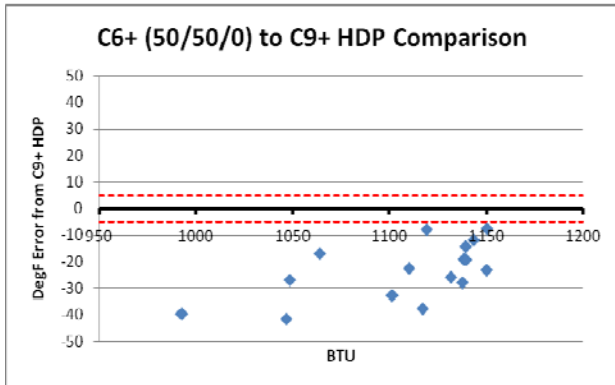
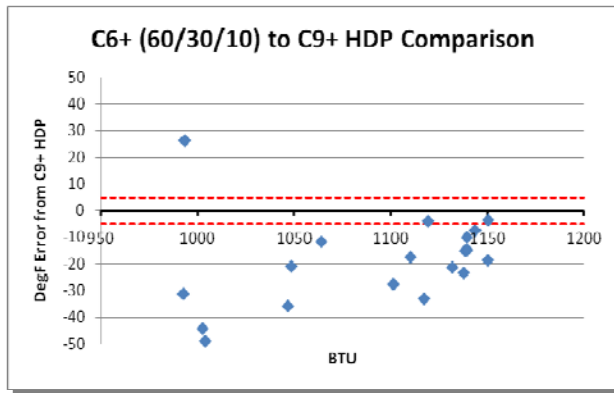
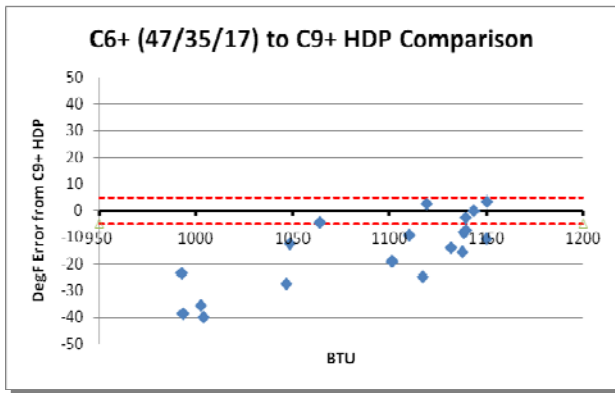
To provide a measurement of the true split of the C6+ composition, the C9+ GC was developed. The C6+ component is analyzed separately and the hexanes, heptanes and octanes concentrations are reported individually, and the heavier components are reported as a C9+ value. The HDP Calculation can then performed in the GC controller, to provide a continuously online HDP measurement.

To illustrate the errors that using fixed ratios of the C6+ component to calculate the HDP, the HDP for large sample of extended natural gas composition analysis results was calculated using a C9+ analysis and the various ratios for the C6+ component. The errors between the C9+ HDP value and the HDP calculated for the fixed C6+ ratios shows that none provides a viable calculation with any acceptable accuracy (refer Figure 2 - C9+ HDP to C6+ Ratio HDP Errors.) The charts show the error in degrees Fahrenheit on the y-axis, and the BTU content on the x-axis.

In most cases, using a fixed ratio of a C6+ measurement results in a value under the HDP calculated with a C9+ analysis. This is a major operational issue for pipeline operators who wish to control the gas in their pipelines below a tariff nominated value. If the HDP is under-reported, gas with an true HDP higher than the tariff limit

may enter the network even though the “reported” HDP is well below the limits.

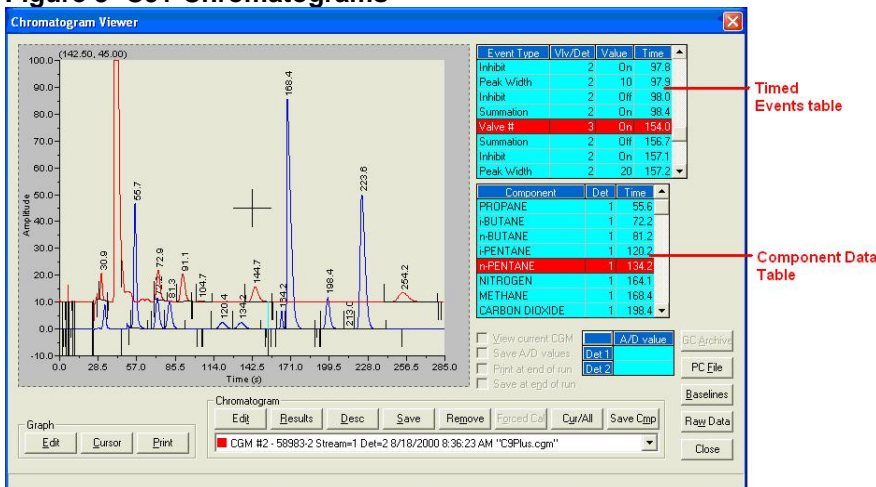
**Figure 2 - C9+ HDP to C6+ Ratio HDP Errors**



### C9+ Chromatography

The extended C9+ analysis is achieved by performing a parallel analysis application. On one analytical path, the C1 to C5 components, nitrogen and carbon-dioxide are measured. On the second analytical path the heavier components are grouped into hexanes, heptanes and octanes, with the components larger than n-octane back-flushed to provide a C9+ grouped component value. Both analytical path's detector outputs are displayed on the chromatogram viewer simultaneously. In the snapshot shown in Figure 3, the C1 to C5, carbon-dioxide, and nitrogen analysis is shown with the blue trace. The heavier components that have been further split into hexanes, heptanes, octanes and C9+, is shown in Figure 3 with the red trace.

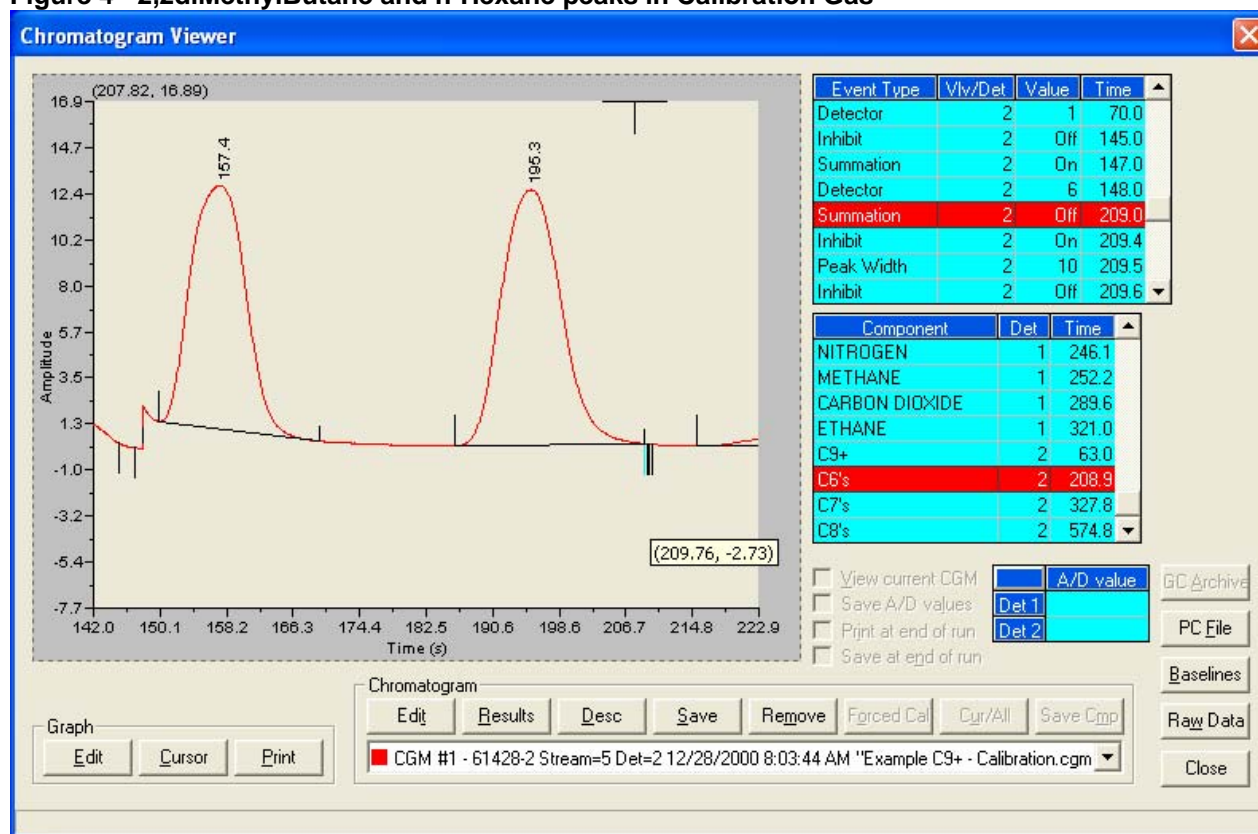
Figure 3- C9+ Chromatograms



As the carbon-number of a hydrocarbon group increases, the number of possible isomers increases and the separation, calibration, and measurement of each individual isomer is impractical. To overcome this limitation, the measurement of the heavier components is performed using a summation process. When using a summation, the beginning and end of the isomers for the grouped component is defined, and any peak that is measured in between these is summed to provide the value of the grouped component. Nominating the ratio of the individual isomers for a grouped component is also possible using the software loaded into the GC Controller, which will be discussed later in the paper.

The chromatography columns used in the C9+ GC perform the separation of the individual components by the boiling point of each component. Components with a low boiling point will elute from the columns before components of a higher boiling point. In the case of the hexanes group, 2,2 dimethylbutane has the lowest boiling point (121.46 DegF – 49.7DegC) and normal-hexane has the highest boiling point (156.2 DegF – 69 DegC). Therefore, by using these two components in the calibration gas, the start and end of the hexanes group can be defined. Any component that elutes between these two is included in the summated hexanes value. These peaks are shown on the chromatogram viewer for a typical calibration gas analysis in Figure 4. The start and end of the grouped components is defined by the SUMMATION ON and SUMMATION OFF times that is shown in the Timed Events table at the top right of the Chromatogram viewer.

**Figure 4 - 2,2diMethylButane and n-Hexane peaks in Calibration Gas**



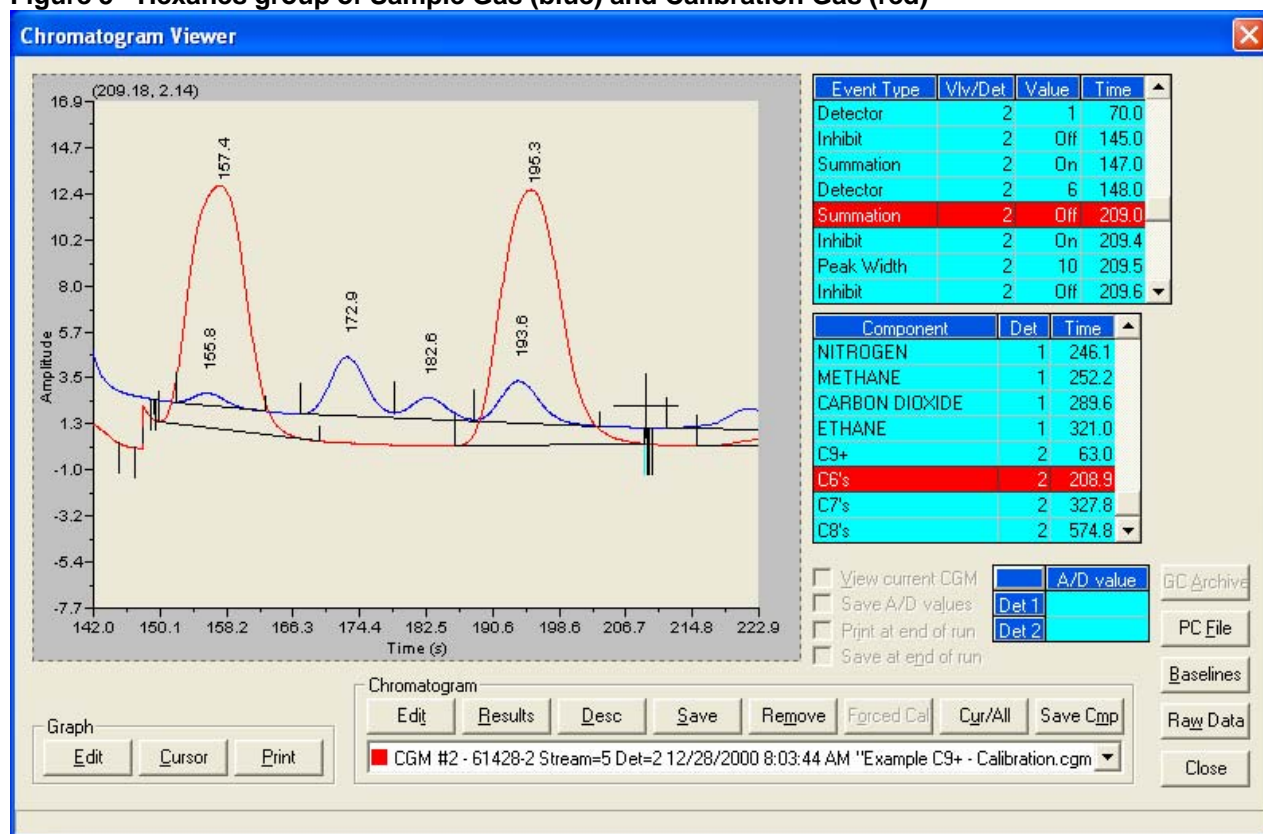
For individually measured components (such as methane, ethane, etc.) the component is identified by the *retention time*. The actual retention time for each individual peak, for that analysis run, is shown on the chromatogram above the measured peaks. The expected retention time (set during a calibration run) for each component is shown in the *component data table*, on the right of the chromatogram viewer.

However, for a grouped component used in the C9+ analysis, the retention time defined in the component data table is set to the time of the SUMMATION OFF, as this is what defines the end of the group of components. A common cause of mis-measurement in a C9+ GC is when the retention time defined in the component data table is for the n-hexane peak and not for the SUMMATION OFF time, resulting in the reported hexanes value for the analysis run being only the n-hexane component, rather than the entire hexanes group. This error will yield lower than expected values and thus lower than expected HDP results.

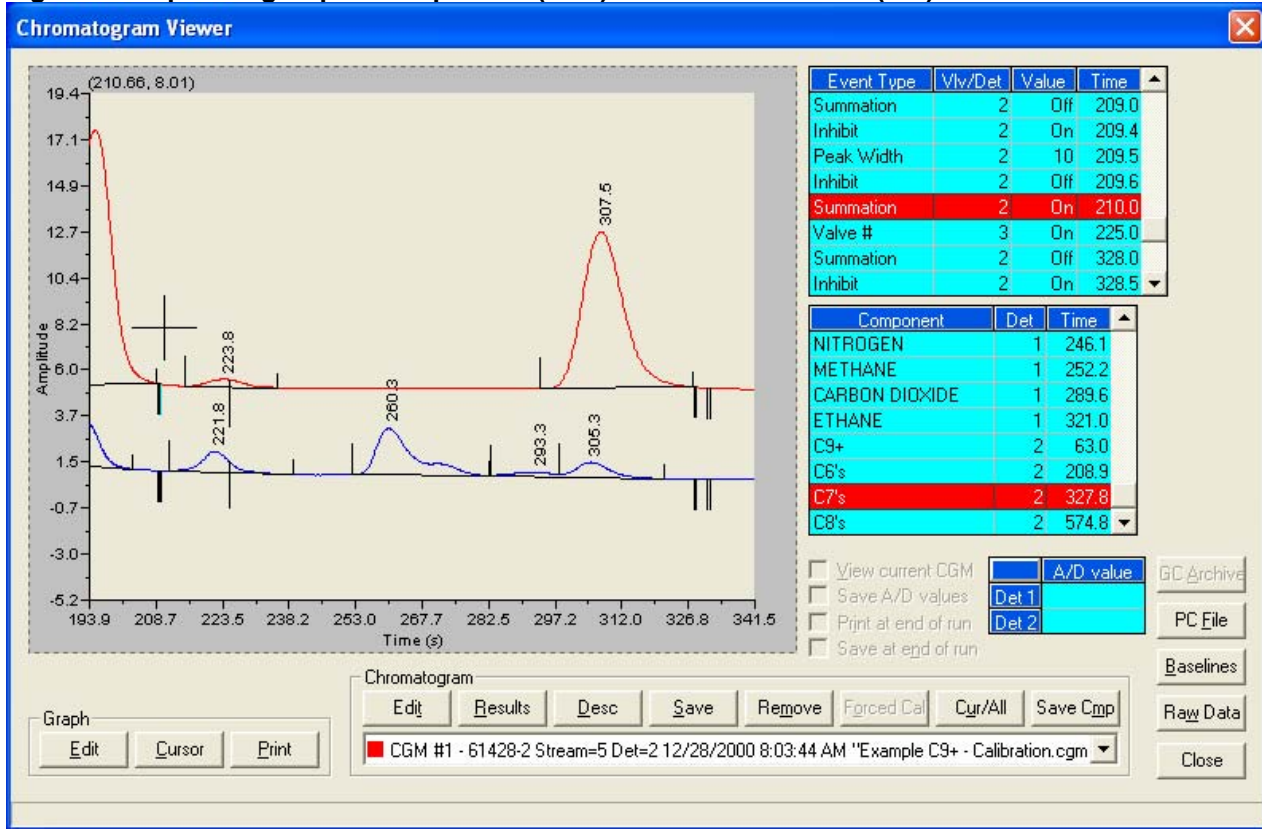
Figure 5 shows the hexanes group of a “typical” pipeline quality gas (Blue) with the calibration gas analysis superimposed in red. Note that there are many other components in the sample gas between the two peaks detected in the calibration gas. Whereas it is theoretically possible to define every component individually in the gas, this would require the each component to be identified and calibrated for, a complicated and expensive proposition. As the carbon number rises, the number of possible isomers and other components (for example, aromatics) that are summed for a carbon number group begins to rise dramatically. To fully separate all these individual components into separate peaks and allow the absolute definition of each peak requires a long analysis time (typically over 50 minutes) and is impractical for the use in online metering systems. By defining the start and end of the grouped components in the calibration gas and summing all of these peaks as a grouped component, an accurate and practical measurement of any component that happens to be in the pipeline is achieved.

For the heptanes and octanes group, only the normal component is used in the calibration gas to identify the end of that grouped component because the start of the heptanes or octanes grouping is immediately after the end of the previous grouping, which has been defined by the normal component in the calibration gas. This is shown for heptane in Figure 5, in which the end of the hexanes group is defined by the SUMMATION OFF time of 209 seconds, and thus the SUMMATION ON time for the heptanes group is set to 210 seconds.

**Figure 5 - Hexanes group of Sample Gas (blue) and Calibration Gas (red)**



**Figure 6 - Heptanes group of Sample Gas (blue) and Calibration Gas (red)**



**Dew Point Calculation configuration**

The dew point calculation module in the controller will calculate the HDP four defined pressures (in PSIA or BarA) and the cricondentherm temperature and pressure for each stream.

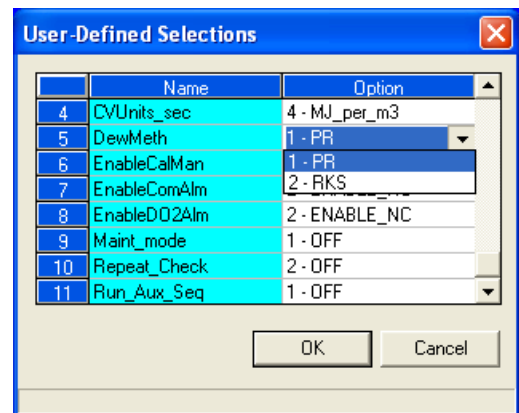
The equation of state used in the calculation can be selected between the Redlich-Kwong-Soave or Peng-Robinson methods with the DewMeth parameter in the "User Defined Selections" table as shown in Figure 7.

The pressures at which the dew point calculations are performed is configured in the "User Defined Numerics" table as shown in Figure 8. These values are always entered in absolute units (PSIA for U.S. applications, BarAbs for metric applications.) The results for the calculation also appear in the "User Defined Numerics" table, along with the "Error Status" of the calculations.

The error status conditions for the calculations are:

- 0 = Calculation is valid.
- 1 = Err1 - No valid solution to gas equation found. Often due to incorrect or unrealistic Pressure setting, such as 0 PSIA or 0 BarA.
- 2 = Err2 - mole% values are all zero.
- 3 = Err3 - calculated fugacities too large - unrealistic composition
- 4 = Err4 - Single phase, no liquid phase at this pressure
- 5 = Err5 - Pressure Value is negative

**Figure 7 – Equation of State Calculation selection**



- 6 = Err6 - No Maximum found (Cricondentherm only)

All these values are available on a modified SIM\_2251 Modbus Map, or for configuration for a user defined modbus map.

**Figure 8 - User Defined Numerics table**

	Name	Type	Value
2	DewPres1	Float	40
3	DewPres2	Float	50
4	DewPres3	Float	30
5	DewPres4	Float	1.1
6	DewStat1	Integer	0
7	DewStat2	Integer	0
8	DewStat3	Integer	0
9	DewStat4	Integer	0
10	DewTemp1	Float	0
11	DewTemp2	Float	0

Single-precision floating point field (For Help, press F1)

### **Group Component Characterizing**

Further customization of the calculation is possible by “characterizing” the grouped components to split the grouped components into fixed ratios for individual components. The ratios used can be determined by an extended analysis from a Spot or Composite sample, and will provide an online HDP calculation comparable to results obtained from an offline extended analysis previously only possible by using an external calculation package and a one-time spot sample.

Caution must be used when using this customized characterization. Whereas the ratio of the individual components may hold true for an individual producer, the different gas qualities and production methods used by all the suppliers to a gas pipeline will almost certainly be different. Therefore the ratios found in the final gas mix will change depending on the production rates and quality of all the suppliers. For this reason, a customized characterization will only be valid for a single source producer and is not recommended for the delivery points at the end of a multiple supplier pipeline.

The default characterization is conservative, entering the grouped components into the equation of state calculations as the normal components (i.e. hexanes = n-Hexane, heptanes = n-heptanes, octanes = n-octanes). As the HDP is used as a protection against liquid drop-out, the use of this default characterization is sufficient for general use, and allows for a consistent method of calculation at all points in the chain of custody.

The use of a customized characterization does result in a small improvement of the reported HDP, and can be configured in the “User-Defined Numerics” table of the GC configuration. There are 92 separate components that can be defined for use in the calculation. For ease of use, they have been separated into 15 different groups:

- a - Natural gas components up to C5
- b - C6 Isomers
- c - C7 Isomers
- d - C8 Isomers
- e - C9 Isomers
- f - C10 Isomers
- g - normal heavy alkanes nC10 - nC18
- h - non-organics
- i - dienes and arenes
- j - alcohols
- k - mercaptans
- l - cycloalkanes
- m - alkenes
- n - alkynes
- o - glycol

Each of these components can be defined as a measured component, or as a fraction of a measured component. To define a gas as a measured component, the gas is assigned the number x.0, where x is the component



number in the Component Data Table (See Figure 9). In the example shown, the user defined numeric entry for n-pentane would be 5.0.

**Figure 9 - Typical C9+ Component Data Table**

Component Data Table 1 (Total Concentration = 100.00000%)

#	Component	Usr/Std	Det ID	Ret Time	Resp Factor	Fxd/Var	Calib Conc	Anly Meth	RT Sec Dev	RT Upd Meth	Resp Fact %
1	PROPANE	Std	1	53.0	1244970	Var	1.008%	Area	4	Cal	10
2	i-BUTANE	Std	1	68.9	1435859	Var	0.3%	Area	4	Cal	10
3	n-BUTANE	Std	1	78.0	1491547	Var	0.3%	Area	4	Cal	10
4	i-PENTANE	Std	1	115.8	1620488	Var	0.1%	Area	6	Cal	10
5	n-PENTANE	Std	1	129.4	1684300	Var	0.1%	Area	6	Cal	10
6	NITROGEN	Usr	1	160.4	709935	Var	2.5059%	Area	2	Cal	10
7	METHANE	Std	1	164.9	583736	Var	89.5751%	Area	3	Cal	10
8	CARBON DIOXIDE	Std	1	194.5	848394	Var	1.001%	Area	6	Cal	10
9	ETHANE	Std	1	219.6	950543	Var	5%	Area	6	Cal	10
10	C9+	Usr	2	31.4	9086340	Var	0.01%	Area	3	Cal	10
11	C6's	Usr	2	94.2	6228730	Var	0.06%	Area	3	Cal	10
12	C7's	Usr	2	151.8	8139801	Var	0.02%	Area	3	Cal	10
13	C8's	Usr	2	269.5	8422550	Var	0.02%	Area	3	Cal	10

Std Comps (F2)... Std Values (F3)... Raw Data (F4)... Update STD (F5) Sort RT (F6) OK Cancel

Alphanumeric field (For Help, press F1)

To define a gas as a fraction of a measured component, which is usually done for the grouped components, the gas is assigned a number in the form  $x.fff$ , in which  $fff$  is the fraction of the of the component number  $x$  in the component data table.

For example, if the extended analysis was to show that the hexanes group was composed of:

- 15% 2,2 dimethylbutane
- 75% normal-hexane
- 5.5% methanol
- 0.5% 2,3 dimethylbutane

As Hexanes is component number 11 in the Component Data Table, the operator entries in the user defined numeric tables for these components would be:

- 11.15 2,2 dimethylbutane
- 11.75 normal-hexane
- 11.055 methanol
- 11.005 2,3 dimethylbutane

When configuring the characterization of the grouped components, it is important to understand where the individual components will be seen in the analysis. As the columns separate the components according to the boiling point, where the component will elute can be determined by where the boiling point lies in relation to the normal components.

**Table 3 - Component Groupings by Boiling Point**

Group	Component	Boiling Point		Group	Component	Boiling Point	
		DegF	DegC			DegF	DegC
<b>Hexanes Components</b>							
b	22dimethC4	121.46	49.7	J	Methanol	149	65
b	23dimethC4	136.4	58	M	2m2ptene	153.14	67.3
b	2methylC5	140.54	60.3	B	NC6	156.2	69
b	3methylC5	145.94	63.3			32	
<b>Heptanes Components</b>							
l	MethCycC5	161.24	71.8	C	33dimethC5	186.98	86.1
j	Ethanol	173.3	78.5	C	23dimethC5	193.64	89.8
c	22dimethC5	174.56	79.2	C	2methylC6	194	90
i	Benzene	176.18	80.1	C	3methylC6	197.6	92
c	24dimethC5	176.9	80.5	C	3ethylC5	200.3	93.5
l	CycloC6	177.26	80.7	M	1heptene	200.48	93.6
c	223trimC4	177.62	80.9	C	NC7	209.12	98.4
m	CycHexene	181.4	83				
<b>Octanes Components</b>							
d	224trimC5	210.56	99.2	D	234trimC5	236.12	113.4
l	MethCycC6	213.62	100.9	D	3methylC7	239	115
l	EthylCycC5	218.3	103.5	J	1Butanol	242.96	117.2
d	22dimethC6	224.24	106.8	D	2methylC7	243.68	117.6
d	25dimethC6	228.2	109	D	34dimethC6	243.86	117.7
d	223trimC5	230	110	D	4methylC7	243.86	117.7
d	24dimethC6	230	110	M	1hexene	250.34	121.3
i	Toluene	231.08	110.6	M	1octene	250.34	121.3
d	33dimethC6	233.6	112	E	225trimC6	255.2	124
d	23dimethC6	235.4	113	D	NC8	258.26	125.7

Any component that has a boiling point higher than n-octane (258.26 DegF - 125.7 DegC) will be grouped with the C9+.

### **Conclusion**

In conclusion it can be seen that for a continuous online calculation of HDP, an analyzer with an extended analysis is required. The fixed ratios commonly used for energy calculations in a C6+ GC are not suitable for a HDP calculation because of the disproportionate effect of the heavier components on the HDP result.

The C9+ GC can be used to measure the true ratios of the heavier components that will provide meaningful and useful results from either of the two accepted equations of state. Whereas customization of the individual heavy component ratios for use in the equations of state is possible, because of the large variety of processes used to produce "pipeline quality" gas this is not practical where multiple sources of gas for a system exist.

For applications in which a single source of gas exists, then customization of the component ratios for the grouped components can easily be configured by using the results of an offline extended analysis from a representative sample.