On the correlation between Isothermal Compressibility and Isobaric Expansivity
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ABSTRACT

Fluid properties are a critical element to the success of any pipeline simulation. In some cases the pumped fluid or liquid mixture is so exotic in nature that laboratory data is unavailable and an educated guess is the only course of action. For transient simulation, knowledge of the isothermal compressibility is important and some estimate could be made by realizing the composition of the mixture. For steady state simulation, possibly for a batched system, the flow rates would need to be corrected to standard or pipeline base conditions, and these correction factors require knowledge of both the isothermal compressibility and the thermal expansion properties. If one can estimate the fluid compressibility with some certainty, can one also estimate the isobaric expansivity? Laboratory test data tend to show that liquids with high compressibility also seem to have high isobaric expansivity, indicating a correlation between the two. Hence this paper intends to discover what, if any, correlation exists through examination of fluid properties of known pure components, and application of physical processes and required thermodynamic stability.

NOMENCLATURE

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<tr>
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<td>( a )</td>
<td>Attractive force coefficient</td>
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<td>( v )</td>
<td>Specific volume</td>
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<td>( P )</td>
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<td>( \beta_p )</td>
<td>Isobaric Expansivity</td>
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<td>( R )</td>
<td>Ideal Gas constant</td>
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<td>( \omega )</td>
<td>Acentric factor</td>
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<td>( \chi )</td>
<td>Ratio of isobaric expansivity to isothermal compressibility</td>
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Subscripts

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INTRODUCTION

The total change in either pressure or specific volume in a fluid can be described by two important fluid properties: isobaric expansivity and isothermal compressibility. Isobaric expansivity is used to express the thermal expansion experienced by fluids and is defined as the volume change of a fluid due to temperature change, while holding pressure constant [3]:

\[
\beta_{P} = \left( \frac{1}{V} \right) \left( \frac{\partial V}{\partial T} \right)_{P}
\]

This is also referred to as the coefficient of thermal expansion. The isothermal compressibility is the volume change of a fluid due to pressure changes at constant temperature is defined by:

\[
\beta_{T} = -\left( \frac{1}{V} \right) \left( \frac{\partial V}{\partial P} \right)_{T}
\]

And it can be shown that for thermodynamically stable states [3] that

\[
\left( \frac{\partial P}{\partial V} \right)_{T} < 0
\]

Hence the isothermal compressibility will always be a nonnegative number.
This represents the inverse of the isothermal bulk modulus of elasticity for the pipelined fluid. A general observation for liquid phase is that as the compressibility increases, the thermal expansion also increases. This leads one to wondering if there is a direct correlation between these two fluid properties, and what that might mean for fluids in general.

To arrive at a meaningful relationship this property needs to be combined with an appropriate equation of state in order to show the details of the correlation and help explain the mechanisms involved.

We begin by looking at experimental data provided by the National Institute for Standards and Technology (NIST) [4] for various hydrocarbons used in the pipeline industry, which are typically compounds not pure elements. All fluid property data presented is taken from NIST. The NIST database uses a variety of equations of state, including their “extended corresponding states model” and Helmholtz energy equations of state, including international standard equations for water, carbon dioxide, ammonia and others.

Since pipeline coatings typically define limits of the maximum fluid temperature, and there is a wide variation in acceptable limits. The high limit for temperature was selected to be 580 °R (or 121 °F). Liquid pipeline operations typically have pressure in the range 145 to 1450 psia, so that range was selected for this study.

Furthermore, we need to make the distinction between polar and nonpolar molecules. A polar substance has an electric dipole or charge on its molecules and it may lead to different results from nonpolar substances. Water and ammonia (NH₃) are examples of polar substances and are included in this study. Nonpolar molecules examples include the alkanes, such as methane and ethane, and alkenes such as ethene.

**EXPERIMENTAL RESULTS**

NIST [4] provides various databases of fluid properties, which are based on experimental data.

Table 1 shows a variety of hydrocarbons selected at pressures to ensure liquid phase at a temperature of 540 °R (81 °F). Figure 1 then shows this data plotted with thermal expansion as a function of compressibility. As can be seen there clearly is a one-to-one relationship between compressibility and thermal expansion, for liquid phase. Also, zero compressibility appears to correspond with zero thermal expansion.

The intention of this paper is to explain and predict this correlation from a theoretical basis.

In the next section various hydrocarbons, in order of increasing molar mass, are presented along with some observations about those fluids.

Data is graphed with isothermal compressibility as the independent variable and isobaric expansivity as the dependent variable on the Y axis. Each data point has a given pressure and temperature value, with NIST REFPROP database [4] providing the specific volume, isothermal compressibility and isobaric expansivity for the selected hydrocarbon. Pressure is 145 to 1450 psia in steps of 15 psia. This paper uses absolute scales for pressure, and temperature in degree Rankine.

**Ammonia**

Figure 2 has the liquid phase isotherms graphed for ammonia at three temperatures. The highest pressure point has the lowest compressibility and expansivity values. Following the isotherm as the compressibility increases, the expansivity also increases. As temperature increases the isotherms move to the right. The critical point for this polar molecule is \( T_c = 729 \, ^°R \), \( P_c = 1636 \, \text{psia} \).

**Water**

The critical point for water is \( T_c = 1165 \, ^°R \), \( P_c = 3203 \, \text{psia} \) and Figure 3 shows water for several temperatures below the critical values. At 540 °R the isobaric expansivity decreases with increasing compressibility. Then as the temperature increases, this behavior changes and isobaric expansivity increases as compressibility increases. Water is a polar molecule.

**Ethane**

Figure 4 shows curves for Ethane for three different temperatures for the range of pressures. The highest pressure point has the lowest compressibility and expansivity values and liquid phase. Following each isotherm, left to right, for increasing compressibility the pressure drops. High pressures result in liquid phase and linear variation, as compressibility increases, isobaric expansivity increases, and then dramatically increases until the phase transition to vapor phase occurs, where expansivity starts to decrease while compressibility increases. The critical point for Ethane is \( T_c = 550 \, ^°R \), \( P_c = 708 \, \text{psia} \).

**Carbon Dioxide**

Figure 5 shows the linear molecule CO₂ for four isotherms for pressures ranging from 145 to 1450 psia. Each isotherm starts out showing that expansivity increases somewhat linearly and then loops around and back and then continues on decreasing thermal expansion as the compressibility increases. The low
compressibility linear part of the curve occurs in liquid phase, followed by the transition from liquid to gas and it’s clear that for gas phase one can have as many as three values for isobaric expansivity for a single isothermal compressibility value. The critical point for CO$_2$ is $T_c = 547 \ ^\circ R$, $P_c = 1070 \text{ psia}$.

**Propane**

Values for propane ($T_c = 665 \ ^\circ R$, $P_c = 616 \text{ psia}$) are shown in Figure 6. Higher temperatures resolve the curve more fully than at lower temperatures, where a break occurs and the transition is not apparent. The curves are very similar as in the case of the CO$_2$ and ethane data.

**Octane**

Figure 7 shows Octane at 540 $^\circ R$, which has its critical point at $T_c = 1024 \ ^\circ R$, $P_c = 360 \text{ psia}$. Clearly this is liquid phase only for the pressure and temperature range. Expansivity increases as isothermal compressibility increases. As temperature increases these curves move to the right. For these temperatures and pressure range only liquid phase is experienced.

**Normal Butane**

Figure 8 has n-Butane values ($T_c = 765 \ ^\circ R$, $P_c = 551 \text{ psia}$) shows that each isotherm has expansivity increasing as compressibility increases. The slope of the curve decreases as temperature increases. If the temperature continued to increase the phase change from liquid to gas is expected to occur.

**Comparisons**

Figure 9 shows various hydrocarbons at 540 $^\circ R$ (81$^\circ F$) for liquid phase. They all appear to follow the same curve. This is an interesting result because it implies that a similarity law exists. However Carbon Dioxide interestingly appears to follow a different curve. Ethene or Ethylene follows more closely but also appear to be on a slightly different curve.

**SUMMARY OF RESULTS**

To summarize the discussion of results above:

- A common correlation appears to exist at constant temperature
- Liquid and gas phases have different behaviors
- Isobaric expansivity appears to increase dramatically during the phase change, followed by a decrease.
- Liquid phase has one-to-one relationship with isobaric expansivity increasing as compressibility increases, except for water which exhibits a change of slope. Of the hydrocarbons studied here, water has the lowest compressibility and expansivity values.
- In liquid phase, they all exhibit a monotonically increasing relationship between the isobaric expansivity and the isothermal compressibility; for water the relationship is either increasing or decreasing depending on the temperature.
- The liquid phase curve appears to extrapolate to indicate that zero compressibility corresponds with zero isobaric expansivity.
- The phase change appears to have two or even three values for isobaric expansivity for a single isothermal compressibility value.
- For liquids, the less compressible a substance is the more closely a common isotherm is followed.

**THEORY**

The next step is to see if theory can predict these results. The classical thermodynamic perspective is preferred in this paper over the statistical viewpoint.

**Classical Perspective**

The full or substantive derivative of change in pressure is given by:

$$dP = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT$$

Where the total pressure change is a function of change in volume and temperature and the following relationship can be derived:

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V$$

From the definitions for thermal expansion and isothermal compressibility, it can be shown that the ratio of our two properties of interest leads to a third property - which is the pressure change with temperature change at constant volume:

$$\chi = \frac{\beta_P}{\beta_T} = \frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial T}\right)_T}$$

This can be used with an equation of state to show the nature of the relationship. In this paper we need to trade state equation accuracy with visibility to the underlying physical processes. With this in mind we choose the van der Waals concept buried in every cubic equation of state. The idea that the pressure of fluid results from the sum of repulsive and attractive forces was first expressed by van der Waals in his
equation and indeed all cubic equations are of the “van der Waals” form:

\[ P = P_{\text{repulsive}} + P_{\text{attractive}} \]

The van der Waals equation of state is:

\[ P = \frac{RT}{v - b} - \frac{a}{v^2} \]

The first term on the right side represents the repulsion: the pressure exerted due to collision and is proportional to the thermal part of energy (the sum of the translational, vibrational and rotational energies) of all the molecules within unit volume of free space. The second term is the reduction in force due to the attractive force exerted on those molecules by neighbouring molecules.

We note this repulsive part of pressure is actually a correction over the Ideal Gas equation where the apparent or molecular body volume \( b \) of the molecules is subtracted from the geometrical volume, resulting in a higher value for the pressure. Also the ideal gas equation does not account for the attractive forces that are significant when the molecular spacing is relatively close, like at higher pressures or in liquid phase. The attractive forces serve to reduce the pressure.

This gives only a qualitative description of the repulsive behavior of molecules and the repulsive and attractive contributions are not truly separated [1]. Since the van der Waals equation is not sufficiently accurate for predicting liquid phase pressures, a more accurate cubic equation can be achieved based on the work done by Peng and Robinson [5]. It should be noted at this point that neither cubic equations nor Benedict Webb Rubin equations can be used to predict with confidence the PVT behavior of polar molecules [1]. Also a complex generalized equation of state such as Starling-Han or Benedict Webb Rubin might be more accurate but lack the ability to discern the physical behaviour.

The Peng-Robinson (1976) [5] equation is:

\[ P = \frac{RT}{v - b} - \frac{a}{v^2} \left( 1 + \frac{RT}{p_c^2} \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right)^2 \]

Where \( a \) is a function of temperature andacentric factor as such

\[ a = 0.45724 \frac{R^2 T_c^2}{p_c^2} \left( 1 + k \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right)^2 \]

And \( k \) is a constant characteristic of each substance [5]:

\[ k = 0.37464 + 1.5422 \omega - 0.26922 \omega^2 \]

And the molecular body volume is:

\[ b = 0.07780 \frac{T_c}{p_c} \]

**Figure 10** shows comparisons for pressure versus volume between NIST and Peng Robinson for Ethene at 540 °R (81°F) – they show very good agreement with the average error less than 2% and the standard deviation of the differences less than 1%.

**PHYSICAL PROCESSES**

Consider the isothermal compression of ethene at 540 °R. As the fluid is compressed the volume decreases while the intermolecular spacing decreases. At larger volumes and lower pressures the first term in the van der Waals equation dominates, the body volume \( b \) and

\[ P \propto \frac{1}{v} \]

**Figure 11** shows components of the pressure due to repulsion (first term) and attraction (second term). As the pressure continues to increase a point is reached where the attractive forces start to become as strong as the repulsive forces. The repulsive forces are always larger, though, to ensure thermodynamic stability. Upon compression the body volume effect (which reduces the space available for movement of molecules) is dominant and results in a higher number density so that the first term dominates, although the attractive force serves to reduce the pressure over what it would have been with only the first term.

The NIST data appears to only show thermodynamically stable states where the pressure continues to increase with decreasing volume and \( \frac{dP}{dT} < 0 \) is always true.

**Figure 12** shows as the pressure increases both NIST and Peng-Robinson, with the density graphed along side. Both NIST and Peng-Robinson show a rise in compressibility followed by a decrease, as the density increases. The phase change occurs when the density changes fastest.

**Figure 13** As the pressure increases both NIST and Peng-Robinson predict a rise in expansivity followed by a decrease during the phase change. This maximum value in isobaric expansivity deserves further analysis, which follows next.

**PEAK EXPANSIVITY**

**Figure 14** shows values for isobaric expansivity for different values for the attractive coefficient \( a \) in the van der Waals equation for a hypothetical substance with

\[ b = 1.27991 \text{ ft}^3/\text{kmol} \]
van der Waals was selected for this part of the study due to its simplicity of form. This plot shows that the van der Waals starts to show this peak value when the attractive coefficient $a$ is increased from zero. The isobaric expansivity is calculated here using,

$$\beta_p = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p = \frac{1}{v} \left( -\frac{R}{v-b} \right) - \frac{R}{v-b} + \frac{2a}{v}$$

Using perturbation method, the peak in $\beta_p$ occurs roughly (zero order approximation) when the volume reaches a value of:

$$v_0 \approx \frac{8ab}{2a - RTb}$$

From this result, we can determine that if there were no attractive forces involved, the isobaric expansivity would show merely a continual decrease as volume increases, going from high pressure liquid phase down to low pressure vapor.

From a pipeline design and operational consideration, volumes around $v_0$ should be avoided as the uncertainty in these properties increases (Figure 15 demonstrates).

It’s clear that the molecular attractive force plays a significant role in how this mechanical property behaves.

If a vapor is compressed, its molecules exist closer to each other. As the intermolecular distance is reduced, the attractive force between adjacent molecules becomes large enough to reduce the molecular velocity. Gas molecules slow down to a state at which matter changes phase and becomes a liquid [3].

We note that this compression process allows for a greater increase in thermal expansion during the phase change than would occur if there were no attractive forces. And, it allows for the behavior noticed with liquid phase: that the expansivity increases with an increase in compressibility.

**PREDICTING RATIOS**

For Peng-Robinson equation, the ratio between isobaric expansivity and isothermal compressibility is:

$$\chi = \left( \frac{\partial P}{\partial T} \right)_v$$

$$= \frac{R}{v-b}$$

$$0.45724 \frac{R^2 T_c^2}{P_c} \frac{2}{v(v+b) + b(v-b)} \left( 1 + k \left( 1 - \frac{T}{T_c} \right) \left( -\frac{k}{2\sqrt{T_c}T_c^3} \right) - \frac{1}{2\sqrt{T_c}T_c^3} \right)$$

Like the van der Waals equation, this implies that the isobaric expansivity and isothermal compressibility are related to each other directly by the effect of the intermolecular attraction and repulsive forces.

**CONCLUSIONS**

One common assumption for liquids is a constant value [3] for isothermal compressibility and isobaric expansion however these results clearly show that this statement does not indicate accurate behavior for hydrocarbons over the specified range of operating pressure and temperature. Figure 17 shows that the correlation for n-Butane in liquid phase is somewhat linear (Figure 18 shows it more clearly) and for gas phase has a hyperbolic fit.

**Liquid Phase**

Liquids show a direct increase in isobaric expansivity with an increase in compressibility, for the same temperature. Also for the same temperature a variety of liquids follow the same curve (see Figure 9). Both repulsive and attractive forces are significant for this state of matter. The molecular body volume effect reduces the space available for movement of molecules which results in reduced compressibility and reduced expansion, as the pressure increases. All of the substances studied here appear to share this behavior, except for water which isn’t a hydrocarbon and which appeared to change slope as the pressure increased. Further study is desirable to explain why water’s correlation has the slope changing to a negative value for higher pressures, and is likely related to its polar nature.

**Phase Transition**

For a liquid at high pressure as the pressure is dropped the compressibility increases and the isobaric expansivity increases as well. This increase in expansivity continues until the phase starts to change where it reaches a maximum value and then begins to decrease. The phase change is characterized by a sudden drop in both repulsive and attractive forces (see Figure 11). The isobaric expansivity continues to drop into the vapor phase as demonstrated by Figure 19 and tends to level off as zero pressure is approached.
Applications

The realism of any pipeline simulation is a direct consequence of the accuracy of the configured fluid properties. This paper provides a guide for inspecting the density gradient properties of isothermal compressibility and isobaric expansivity, showing that a clear relationship between the two properties exists at a single temperature. It also shows that hydrocarbons tend to follow the same curve at a given temperature for liquid phase. For phase changes the isobaric expansivity can change significantly with respect to isothermal compressibility, reaching a peak value before decreasing again. Furthermore the use of constant values for isothermal compressibility and isobaric expansivity should be carefully considered over the range of operating pressure and temperature.

References


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About the Author

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Table 1 – Various hydrocarbons at different pressures, all liquid phase at 540 °R (NIST)
FIGURES

Figure 1 - Isobaric expansivity versus isothermal compressibility for different hydrocarbons at 540 °R

Figure 2 - Ammonia for 160 – 1437 psia for three isotherms
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END OF PAPER