PITFALLS OF CO_2 FREEZING PREDICTION

Tim Eggeman and Steve Chafin
River City Engineering, Inc.
Lawrence, Kansas USA

ABSTRACT

Carbon dioxide (CO_2) and its potential for freezing can be a limiting factor in gas plant design and operation. Feed CO_2 levels can dramatically affect project economics and risk as it may dictate the type of recovery process utilized, the maximum achievable NGL recovery, and/or the amount of amine treating required. The usual approach for avoiding CO_2 freezing conditions uses thermodynamics to make predictions of freezing temperatures at key locations within a given processing scheme. A minimum temperature safety margin is then employed to ensure that CO_2 freezing conditions are avoided.

We have found that unreliable CO_2 freezing temperature predictions are being made by several of the commercial process simulators typically used by gas processors. This sparked the literature review presented here. In general, we found the existing experimental data were adequate and that thermodynamic models, both equation of state and activity coefficient based, can be used to make accurate predictions of CO_2 freezing temperatures. However, previous work has not adequately addressed how to properly apply these models within a process simulation. Improper formulation of the CO_2 freezing calculations was the cause of the unreliable predictions made by the commercial process simulators.

In this paper, we will show how to properly formulate the thermodynamic calculations used to predict CO_2 solids formation. Procedures for heat exchangers, expanders and columns will be discussed. Common pitfalls (convergence to spurious roots, convergence to physically meaningful but useless solutions, non-convergence of numerical algorithms, improper formulation of temperature safety margins, etc.) can be avoided by using these procedures.

PITFALLS OF CO_2 FREEZING PREDICTION

BACKGROUND

River City Engineering was recently contracted to provide process engineering services during the revamp of an existing gas plant to recover additional ethane. For this particular revamp, the overall project economics were extremely sensitive to achievable ethane recovery levels. Moreover, the potential addition of inlet gas amine treating to remove CO_2 would have seriously jeopardized the entire project's viability. Thus our goal was to achieve high ethane recovery despite possible constraints posed by CO_2 freezing in the process equipment.

The gas processed at the facility in question is a lean gas with a fairly high CO_2/ethane ratio. The subcooled reflux process considered for the plant is shown in Figure 1. This process is well known and widely utilized throughout the gas processing industry for economically recovering ethane from a wide range of gas compositions. Figure 1 also indicates the typical locations where, depending upon gas composition, CO_2 content, and operating conditions, CO_2 freezing may occur. Generally, these locations are checked by a design engineer for an approach to CO_2 freezing using built-in process simulator utilities and data published in the GPSA Engineering Data Book [1] as well as other sources.

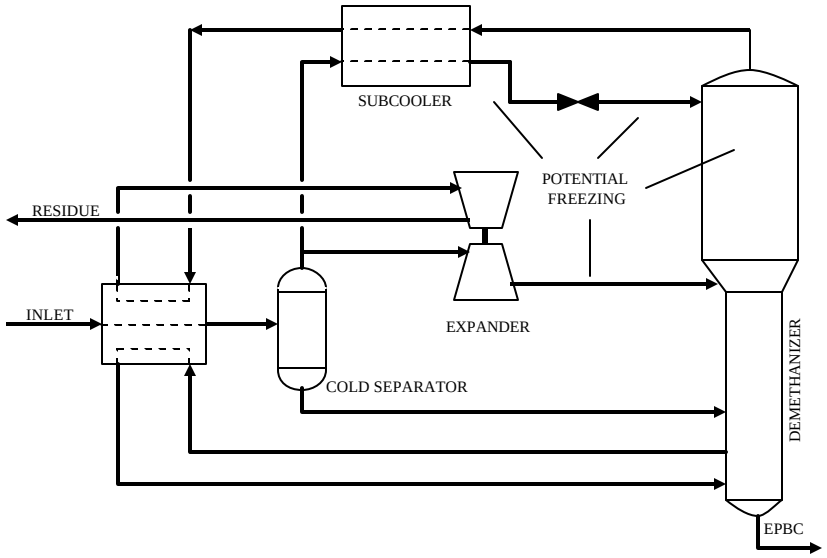


Figure 1 – Ethane Recovery Process Flow Scheme

When the initial revamp design simulation was checked for CO_2 freezing, it was unclear whether our base process simulation package was providing accurate predictions for conditions in the overhead section of the demethanizer tower (Table I). When other process simulation packages were used to provide a comparison, a lack of prediction consistency was observed. Notice the discrepancies between the prediction of the three process simulators as well as to the data commonly referred to in

the GPSA Engineering Data Book, Figure 13-64 [1]. Suspect results were noted for vapor streams in alternate, off-design simulation cases as well (Table I).

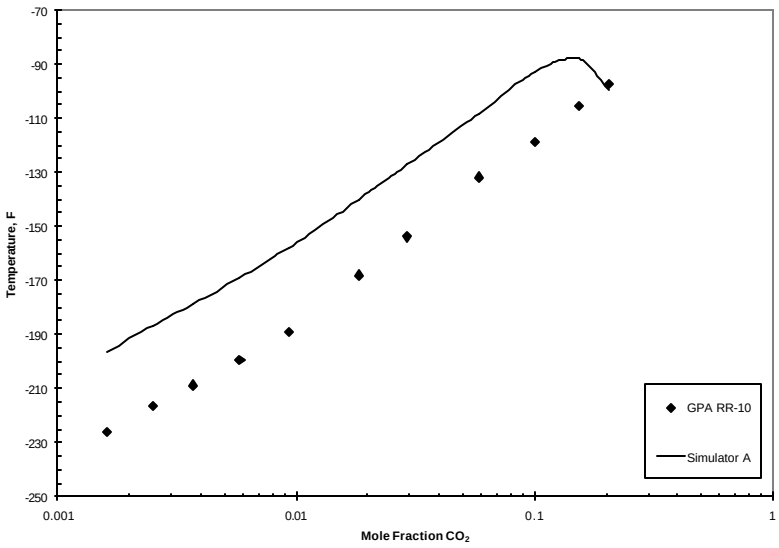
Table I: Liquid and Vapor CO_2 Freeze Comparison

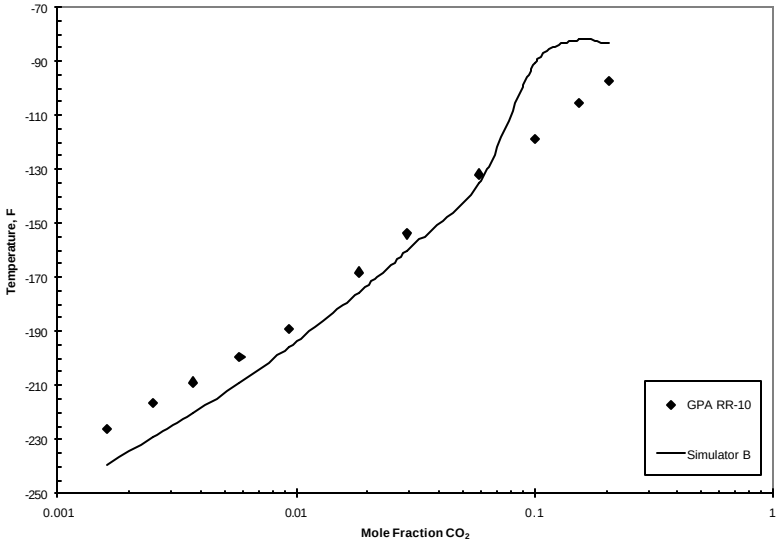
Components (mole%)	Tray 1 Liquid	Tray 2 Liquid	Tray 3 Liquid		Off-Design Vapor
N2	0.38	0.31	0.29		1.42
CO_2	3.44	5.49	6.82		1.13
Methane	90.35	85.64	80.29		96.38
Ethane	5.03	7.65	11.54		1.03
Propane	0.69	0.79	0.92		0.04
C4+	0.11	0.12	0.14		Trace
Simulated Temperature	-152.5°F	-149.2°F	-145.4°F		-137.3°F
Freeze Prediction-Simulator A	-133.5°F	-123.4°F	-123.8°F		-190.3°F
Freeze Prediction-Simulator B	-158.3°F	-121.0°F	-120.9°F		-190.2°F
Freeze Prediction-Simulator C	-159.3°F	-123.4°F	-123.8°F		-190.3°F
GPSA: Figure 13-64	-157°F	-142°F	-134°F		-155°F

These discrepancies led us to examine a simpler case; freeze point prediction for the methane-CO_2 binary system. These predictions can be directly compared with experimental data in GPA Research Report RR-10 [2]. The results for the liquid-solid equilibrium (LSE) comparison are shown in Table II and graphically in Figure 2.

Table II: Methane-CO_2 Binary Freezing Comparison (LSE)

		Temperature (°F)			
Mole Fraction Methane	Mole Fraction CO_2	GPA RR-10	Simulator A	Simulator B	Simulator C
0.9984	0.0016	**-226.3**	-196.3	-239.2	-236.4
0.9975	0.0025	**-216.3**	-186.9	-229.3	-227.0
0.9963	0.0037	**-208.7**	-178.8	-220.1	-218.1
0.9942	0.0058	**-199.5**	-169.0	-208.8	-207.1
0.9907	0.0093	**-189.0**	-158.1	-195.9	-158.0
0.9817	0.0183	**-168.0**	-140.0	-175.5	-140.0
0.9706	0.0294	**-153.9**	-127.3	-159.9	-160.9
0.9415	0.0585	**-131.8**	-108.1	-135.1	-108.1
0.8992	0.1008	**-119.0**	-92.9	-90.8	-92.9
0.8461	0.1539	**-105.2**	-88.1	-82.1	-88.0
0.7950	0.2050	**-97.4**	-99.4	-83.6	-99.4
Maximum Absolute Deviation			31	28	31





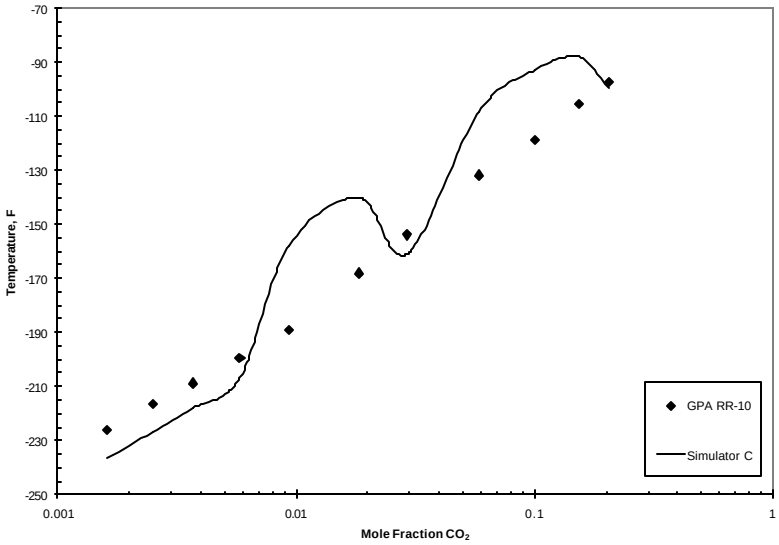


Figure 2 – Comparison of Liquid Phase Methane-CO_2 Freezing Predictions

It is clearly evident that the three process simulators are not reliably matching experimental LSE data for even this simple system. The results were unexpectedly poor. Our need for dependable liquid-solid and vapor-solid prediction sparked the review of existing experimental data, a review of the thermodynamics of solid formation, and the development of the calculation procedures presented in this paper.

LITERATURE REVIEW

There are actually two modes for formation of solid CO_2 in gas processing systems. In one, the CO_2 content of a liquid can exceed its solubility limit, in which case carbon dioxide precipitates or crystallizes from the liquid solution. In the other, the CO_2 content of a vapor can exceed the solubility limit, in which case solid CO_2 is formed by desublimation or frosting.

Liquid-Solid Systems

The GPA Research Report RR-10 [2] and Knapp et. al. [3] are good sources for finding many of the original papers containing experimental data for liquid-solid systems. We were able to obtain the original source papers for most of the data sets, which allowed for critical evaluation. Sources that only contained graphical information were rejected from further consideration because of the limited accuracy of interpolation. We also judged the degree of care used in the experimental methods and traced the sometimes twisted lineage of the data sets to ensure all of the data were independently determined.

We decided to only include the data presented in GPA RR-10 for the regressions discussed later. The data reported in GPA RR-10 are actually a compilation from several sources [4-7]. These data are of high quality. The measurements are based on three phase experiments (vapor-liquid-solid), so the pressure at which the data were collected was recorded. In general, data sets from other sources did not record system pressure. System pressure is needed to correlate the data when using the equation of state approach, as discussed later.

Figure 3 is a plot of experimental data for the solubility of CO_2 in methane. Also shown are experimental data from sources outside [3, 8-10] of those given in GPA RR-10. There is some scatter in the data around -150°F, which is the region of interest for the distillation problem at hand. Unfortunately, we have not been able to devise a meaningful thermodynamic consistency test, similar to those used to examine VLE data, to justify throwing away certain data sets or specific data points.

Experimental data for the ethane-CO_2 binary system [8,11,12], propane-CO_2 binary system [8,11], methane-ethane-CO_2 ternary system [11], methane-propane-CO_2 ternary system [13], ethane-propane-CO_2 ternary system [13], and the methane-ethane-propane-CO_2 quaternary system [13] are available. Many of these data sets were collected by Dr. Fred Kurata and his graduate students at the University of Kansas. The scatter in the data for these systems was lower than that shown in Figure 3 since there are fewer independent sets.

Vapor-Solid Systems

The experimental data for frosting of CO_2 are meager. The Pikaar [14] data set for the CO_2-methane binary is frequently displayed in the literature, for example in Figure 25-6 of the GPSA Engineering Data Book [1], but unfortunately the data were never published outside of Pikaar's dissertation. We could not critically review this work since we have not been able to obtain a copy of his dissertation. No other relevant experimental data sets were found.

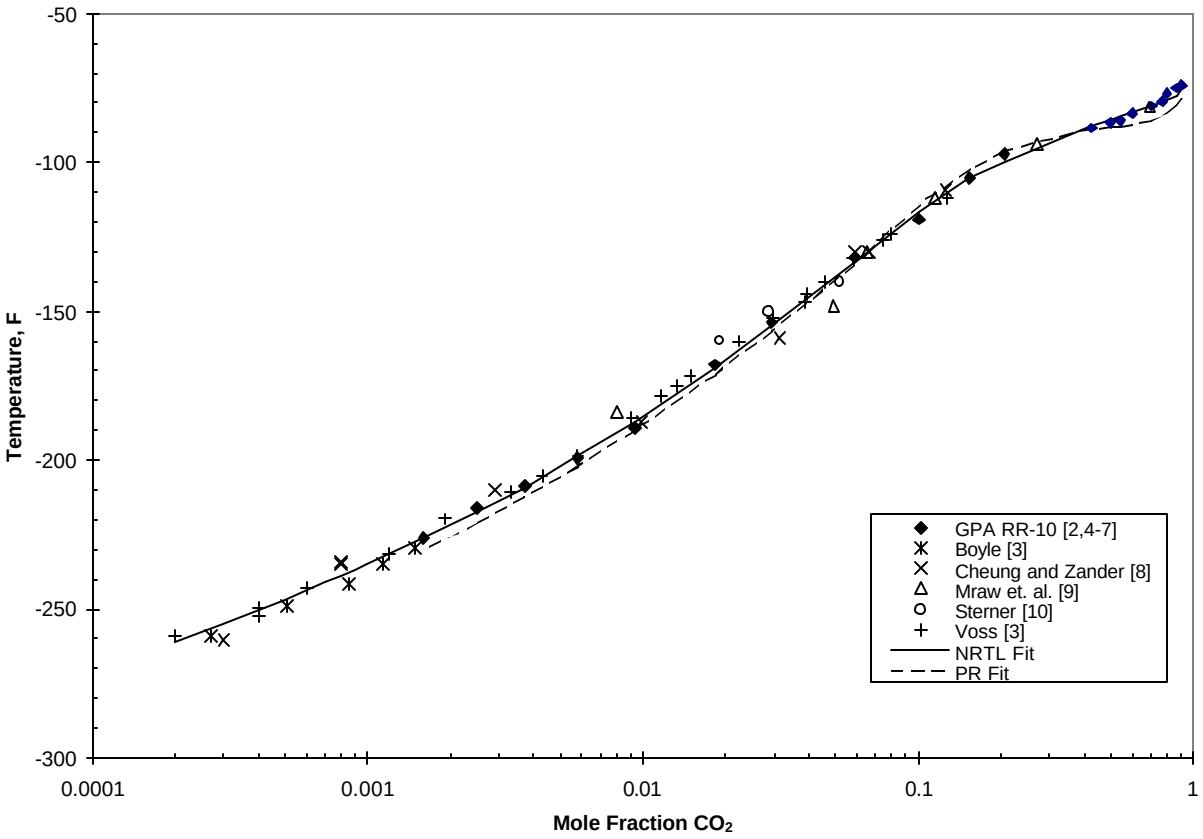


Figure 3 - Solubility of CO_2 in Liquid Methane

THERMODYNAMICS OF SOLID FORMATION

Most of the experimental data were collected in the 1950's-1970's. Computer software and thermodynamic models have advanced since that time. Much of the thermodynamic analysis in the papers containing the original experimental data is dated. This section briefly reviews some modern approaches to correlating the data.

Liquid-Solid Equilibria (LSE)

The starting point in deriving any phase equilibrium relationship is equating partial fugacities for each component in each phase. Only one meaningful equation results if one makes the normal assumption of a pure CO_2 solid phase. Then one has to decide whether to use an activity coefficient or an equation of state approach.

The following equation holds at equilibrium when using an activity coefficient model:

$$\ln g_{CO_2} x_{CO_2} = \frac{(S_{L T_p} - S_{S T_p})}{R}\left(1 - \frac{T_{Tp}}{T}\right) - \frac{((a_L - a_S) - (b_L - b_S)T)}{R}\left(1 - \frac{T_{Tp}}{T}\right) + \frac{(a_L - a_S)}{R}\ln\left(\frac{T}{T_{Tp}}\right) - \frac{(b_L - b_S)}{2R}T\left(1 - \left(\frac{T_{Tp}}{T}\right)^2\right) \qquad (1)$$

where g_{CO_2} = Activity coefficient for CO_2 in the liquid phase, dimensionless

x_{CO_2} = Mole fraction of CO_2 in the liquid phase, dimensionless

$S_{L_{Tp}}$ = Entropy of liquid CO_2 at the triple point, 27.76 cal/(gmol K) [15]

$S_{S_{Tp}}$ = Entropy of solid CO_2 at the triple point, 18.10 cal/(gmol K) [15]

R = Gas constant, 1.9872 cal/(gmol K)

T_{Tp} = Triple point temperature for CO_2, 216.55 K [15]

T = Temperature, K

a_L, b_L = Liquid CO_2 heat capacity = a_L+b_LT = 3.0447+0.0714T, T in K, c_p in cal/(gmol K) [16]

a_S, b_S = Solid CO_2 heat capacity = $a_S + b_ST$ = 5.0745+0.0379T, T in K, c_p in cal/(gmol K) [16]

One interesting feature of Eq. 1 is that the right hand side is independent of composition, so the product $g_{CO_2}x_{CO_2}$ is constant at any given temperature. At -150°F (172 K), $g_{CO_2}x_{CO_2}$ = 0.3036. Assuming x_{CO_2} = 0.05, then g_{CO_2} = 6.07, which indicates a fairly high level of liquid phase non-ideality in the region of interest.

We chose the NRTL equation [17] to model the activity coefficient since it is applicable to multi-component mixtures and is capable of handling the expected level of non-ideality. The binary interaction parameters between methane and CO_2 were regressed using the GPA RR-10 data in Figure 3. The resulting fit, also shown in Figure 3, gives good agreement over the entire range. The absolute value of the maximum deviation from the GPA RR-10 data was 2.6°F, a much closer fit than any of the simulator predictions shown previously in Table II/Figure 2. The absolute value of the maximum deviation from the additional data sets shown in Figure 3 was 9.4°F, reflective of the higher degree of scatter.

We have regressed NRTL parameters to predict CO_2 freezing of liquid mixtures containing methane, ethane and propane. Non-key interaction parameters (e.g. methane/ethane binary) were set by converting Wilson parameters from VLE regressions given in Im [16] into an NRTL format by equating the two models at infinite dilution. The resulting fits are comparable to that shown in Figure 3.

These four components (CO_2, methane, ethane, propane) are responsible for over 99% of the species present in the original demethanizer problem summarized earlier in Table I. The remaining species were mapped into either methane or propane according to boiling point. The error caused by this approximation should be quite small, but it does point to some of the limitations of the activity model approach: 1) limited accuracy of predictive modes for generating key interaction parameters through UNIFAC or similar means, 2) difficulties in handling supercritical components via Henry's law, and 3) the need to generate a large number of non-key interaction parameters.

Switching to an equation of state model, the following equation holds at equilibrium:

$$x_{CO_2}\hat{f}^{L}_{CO_2}P = P^{Sat}_{CO_2Solid}f^{Sat}_{CO_2}e^{\frac{V_{CO2Solid}}{RT}(P-P^{Sat}_{CO_2Solid})} \qquad (2)$$

where x_{CO_2} = Mole fraction of CO_2 in liquid phase, dimensionless

$\hat{f}^{L}_{CO_2}$ = Liquid phase partial fugacity coefficient for CO_2, dimensionless

P = System Pressure, kPa

$P^{Sat}_{CO_2Solid}$ = Vapor pressure of solid CO_2 at system temperature, kPa

$f^{Sat}_{CO_2}$ = Fugacity of pure CO_2 vapor at $P^{Sat}_{CO_2Solid}$, dimensionless

V_{CO_2Solid} = Molar volume of solid CO_2, cm^3/gmol

R = Gas constant, 8314 (kPa cm^3)/(gmol K)
T = Temperature, K

The vapor pressure and molar volume of solid CO_2 were regressed from the data in [15]. Any equation of state could be used to calculate the required fugacities. We chose a standard form of the Peng-Robinson equation [18,19] since it is widely used to model natural gas processing systems. Binary interaction parameters for all of the non-key pairs were set to their values derived from VLE regressions. VLE based interaction parameters can also be used with CO_2 pairs, resulting in surprising accuracy. We have found, though, slightly better performance when the interaction parameters for the CO_2 pairs are regressed from experimental data.

Figure 3 compares the fitted Peng-Robinson (PR) model predictions for the CO_2-methane binary system with the experimental data and the NRTL model predictions. The Peng-Robinson model has accuracy comparable to that of the NRTL model in the -150°F region, but the accuracy falls off in other areas. The CO_2-methane binary interaction parameter only had to be changed by ~13% from the value used for VLE calculations. Frankly, we were quite surprised by the ability of the Peng-Robinson equation of state to accurately model this system given the high degree of non-ideality.

While the equation of state approach has the advantage of providing a consistent theoretical framework that is more easily extended to new situations, the details of the numerical procedures required are more complex. For example, when the Peng-Robinson cubic equation of state is used, one needs to find roots of:

$$z^3 - (1-B)z^2 + (A - 3B^2 - 2B)z - (AB - B^2 - B^3) = 0 \qquad (3)$$

where z is the unknown compressibility, and A and B are real constants that are constructed from the mixing rules. The resulting compressibility is then inserted into the appropriate fugacity equation and then Eq. 2 is root solved to find the conditions (T, P, and composition) where solid CO_2 begins to form.

There are up to three real roots for Eq. 3. One is tempted to solve Eq. 3 analytically using Cardan's rule. However, Cardan's rule can produce meaningless results since it is sensitive to round-off errors under certain conditions [20]. Press et. al. [21] discuss numerical methods to find the roots of polynomials. We have found that eigenvalue based methods work well and accurately provide all three roots, whether real or complex.

It is important to initialize the root finding calculation for Eq. 2 with a reasonably good guess. Eq. 3 may only have one real root and if the initial guess is far off target, the resulting compressibility might correspond to that of a vapor rather than a liquid phase, in which case the root finding calculation will converge to a meaningless answer. Unfortunately empirical root discrimination methods for VLE flashes, such as the method by Poling [22], do not always work well with the liquid-solid and vapor-solid flashes considered here. We have found the best way to avoid this pitfall is to use a conservative numerical root solving method, such as false position, in which the root is always bracketed and to initialize the calculation with the result of a converged solution to the NRTL formulation.

Vapor-Solid Equilibria (VSE)

Equation of state models are best used for this type of system since they readily provide the required terms. The relevant equilibrium relationships are:

$$y_{CO_2}\hat{f}^{V}_{CO_2}P = P^{Sat}_{CO_2Solid} f^{Sat}_{CO_2} e^{\frac{V_{CO_2Solid}}{RT}(P - P^{Sat}_{CO_2Solid})} \tag{4}$$

and

$$T \le T_{Tp} \tag{5}$$

where y_{CO_2} = Mole fraction of CO_2 in vapor phase, dimensionless

$\hat{f}^{V}_{CO_2}$ = Vapor phase partial fugacity coefficient for CO_2, dimensionless

P = System Pressure, kPa

$P^{Sat}_{CO_2Solid}$ = Vapor pressure of solid CO_2 at system temperature, kPa

$f^{Sat}_{CO_2}$ = Fugacity of pure CO_2 vapor at $P^{Sat}_{CO_2Solid}$, dimensionless

V_{CO_2Solid} = Molar volume of solid CO_2, cm^3/gmol

R = Gas constant, 8314 (kPa cm^3)/(gmol K)

T = Temperature, K

T_{Tp} = Triple point temperature for CO_2, 216.55 K [15]

Eq. 4 is derived from equating partial fugacities; Eq. 5 merely states the solid must be stable if formed. Quite often thermodynamic textbooks forget to mention Eq. 5. We have found several cases where solids were predicted from Eq. 4 but the temperature was too high for a stable solid.

As in the liquid-solid case, any equation of state can be used to evaluate the fugacities. We again chose a standard version of the Peng-Robinson equation. This time, due to the lack of data, the binary interaction parameters were defaulted to the values used for VLE calculations. Figure 4 shows the predictions agree quite well with the experimental methane-CO_2 binary data derived from Pikaar [14]. Further improvement by regressing the data was not pursued since the experimental values would have to be interpolated from a second generation graph rather than the original data.

The numerical methods used to solve Eq. 4 for the conditions (T, P, composition) at which frosting occurs are basically the same as those used to solve the LSE relation given in Eq. 2. To avoid the pitfall of an improperly evaluated fugacity, we again recommend using a conservative root finding method, such as false position, but this time the calculation can be initialized with the result of a converged solution to Eq. 4 under the assumption of ideality (i.e. the fugacities and exponential Poynting factor terms of Eq. 4 are set to unity).

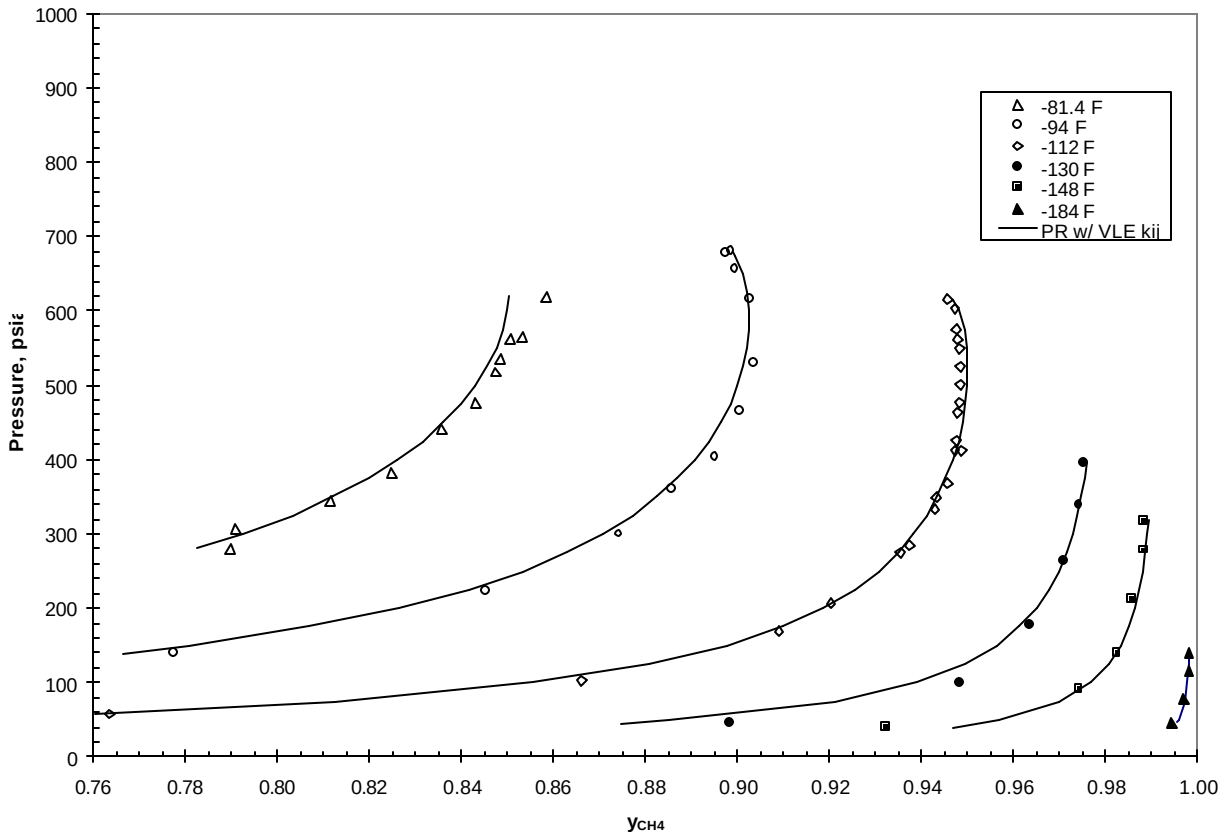


Figure 4 - Frost Point Isotherms for Methane+CO_2 System

CALCULATION PROCEDURES

The usual approach for avoiding CO_2 freezing conditions uses thermodynamics to make predictions of freezing temperatures at key locations within a given processing scheme. A minimum temperature safety margin is then employed to ensure that CO_2 freezing conditions are avoided by allowing for adequate operating flexibility and to account for the uncertainty in the freeze point prediction. We define the temperature safety margin as the temperature difference between the operating temperature and the temperature at which freezing would occur at that phase composition and system pressure. The mechanism for freezing can either be crystallization from a liquid or frosting from a vapor depending upon the type of unit operation. Since understanding the mechanism for freezing is useful information, it is good practice to report whether crystallization or frosting is the limiting factor.

Notice that our definition of the temperature safety margin depends on the phase composition being constant. The CO_2 freeze utility in at least one commercial process simulator is provided in the form of a general purpose stream checker. The problem here is that the utility will perform VLE flash calculations while searching for the nearest freeze point, which changes the phase composition if one happens to be in or near a two phase (i.e. vapor + liquid) region. This not only confuses the issue on how to define the temperature safety margin, but as we will see, introduces the possibility of multiple freeze points and is the source of much of the inconsistent results for that particular simulator.

The next few subsections details how to tailor the thermodynamic calculations to the characteristics of specific unit operations. Our analysis uses thermodynamics with the bulk fluid

properties to predict CO_2 freezing. There are several limitations inherent to this approach. For instance, temperature profiles that occur in the boundary layer when fluids pass over heat exchange surfaces are ignored. It is possible that freezing could occur in the boundary layer but not in the bulk fluid. A second limitation is that thermodynamics does not address the kinetics of nucleation and growth for solid CO_2. It may be possible to operate equipment in regimes where CO_2 freezing is thermodynamically possible, but kinetics inhibit CO_2 freezing. As a third class of example limitations, the actual conditions within a unit operation may not be accurately described by equilibrium thermodynamics. Two cases, one for expanders and one for columns, are discussed later. A more detailed analysis, beyond the scope of this paper, is required if these issues are of concern.

Exchangers

All exchangers, whether a plate-fin or other type of construction, have at least one hot side pass and one cold side pass. To simplify the discussion, we illustrate a CO_2 freezing calculation for a fluid being cooled in the hot side of an exchanger. A cold side analysis follows by analogy.

If the hot side feed is a vapor that does not condense inside the exchanger, then one only has to do a VSE calculation to check the outlet vapor for freezing. Likewise, if the hot side feed is a liquid, then one only has to do a LSE calculation to check the outlet liquid for freezing. The situation becomes more complicated if the hot side feed condenses within the exchanger. In this case, one has to step through the temperature/composition path of the condensing fluid, performing a LSE freezing calculation at each increment.

To see why this is so, consider the hypothetical example shown in Figure 5. The hot feed enters as a saturated vapor (Point A). As it cools, the heavier components preferentially condense, creating a varying liquid phase composition along the exchanger pass. Since CO_2 is heavier than methane, it tends to concentrate in the liquid phase and it is possible to reach a point at which the liquid solubility is exceeded and the CO_2 could freeze and potentially plug the exchanger, shown as Point B in Figure 5. Forget for a moment that the CO_2 could freeze and continue cooling the stream. Eventually enough methane will condense and the CO_2 solubility in the liquid will increase to the point where all of the CO_2 can be held in the liquid phase again without freezing, shown as Point C in Figure 5. If one continues to cool this stream, the vapor phase will completely condense (Point D). Further cooling will eventually cause the liquid solubility to be exceeded again (Point E), where CO_2 could freeze again.

This example shows that multiple freeze points can occur inside an exchanger pass when the process fluid is undergoing a vapor-liquid phase change. In this particular case, just looking at the outlet conditions would lead to the correct conclusion of a freezing problem. However, if the example was modified so that hot side outlet occurred between Points C and E, one would miss the potential freezing problem by looking only at the outlet condition. This pitfall is avoided by the incremental method discussed here.

The example in Figure 5 also explains the inconsistent results from the commercial process simulator that provides CO_2 freeze predictions with a general purpose checker. This simulator does VLE flash calculations on the entire stream while searching for the nearest freeze point. In this case, all three freeze points (Points B, C and E of Figure 5) are thermodynamically valid predictions for the CO_2 freezing temperature. The solution given by this simulator depends upon the internal details of the initial guess and root finding method used by the simulator. As discussed earlier, this pitfall can be avoided by using freeze prediction routines that are customized to a specific unit operation and do not conduct VLE flash calculations while searching for a freeze point.

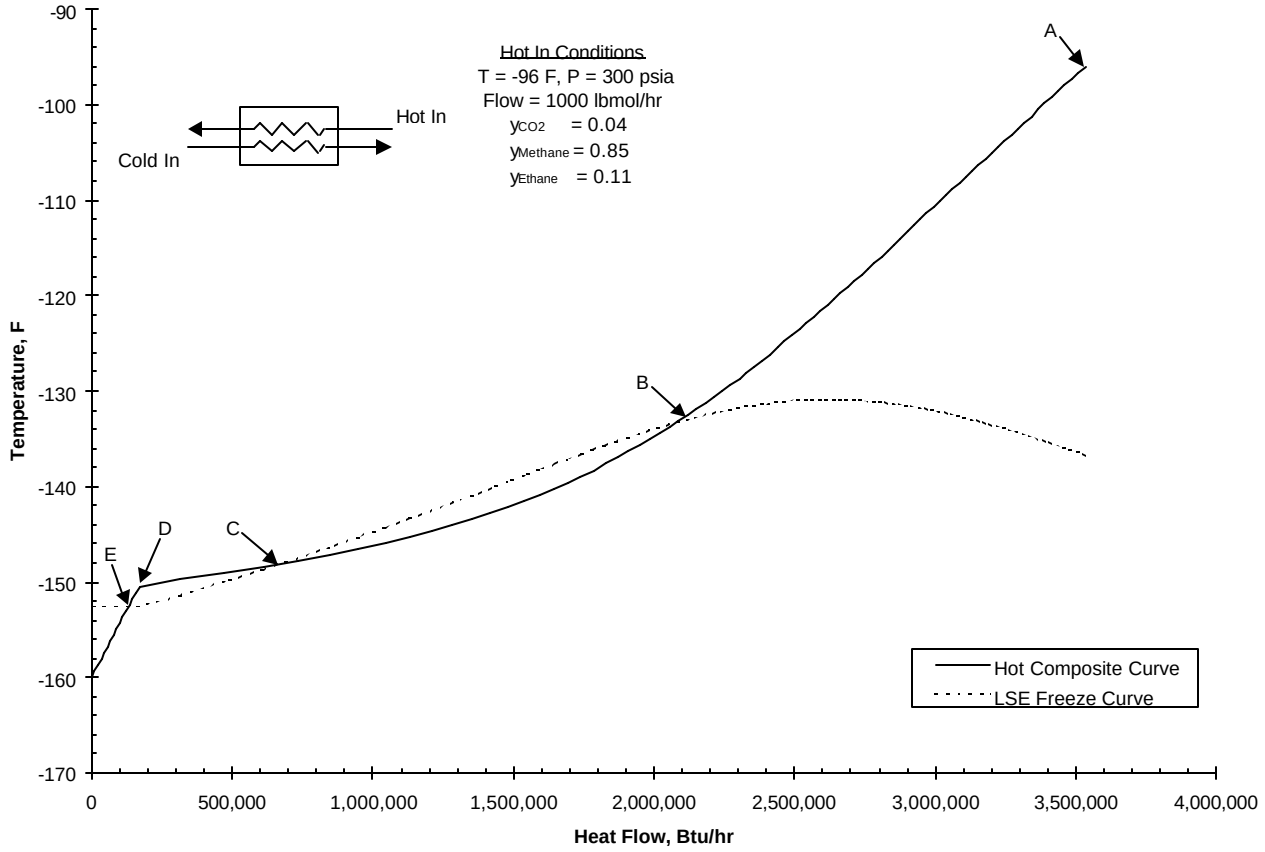


Figure 5 - An Exchanger Profile with Multiple Freeze Points

Expanders

The procedures for prediction of CO_2 freeze points within expanders are similar to those used for exchangers. If there is no phase change within the expander, then one can just do a VSE calculation at the outlet conditions to check for freezing. If condensing occurs within the expander, then an incremental pressure analysis can be performed, checking for freezing with an LSE calculation at each point where liquid exists.

Caveat: In actual operation, when liquid condensation is expected, expanders do not (internally) obey equilibrium thermodynamics. Velocities can sometimes be quite high. There may not be sufficient residence time to truly establish vapor-liquid equilibrium at any given point other than at the outlet. Solid CO_2 formation may also be kinetically limited under these conditions. A more detailed analysis and consultation with the expander vendors should be pursued if this issue is of concern.

Columns

The methodology for CO_2 freezing prediction within columns remains the same as that for any other equipment handling mixed liquid and vapor phases. The evaluation of the approach to CO_2 freezing requires careful analysis and depends upon the type of column under consideration (i.e. packed versus trayed).

General Simulation Issues

A quick review of column simulation is in order before discussing the more specific CO_2 freezing issues. Column operations in the general process simulation packages are tailored specifically to performing stage-wise material and energy balance calculations. These calculations are based upon theoretical column stages. Usually, the design engineer applies a tray efficiency to the actual number of trays to determine the number of theoretical simulation stages for a new or existing column. The actual tray efficiency of a column in operation can be impacted by a number of design, operational, and/or mechanical factors. A similar analogy (via packing HETP) may be applied to packed columns although they are not inherently stage-wise since the vapor and liquid phases are in continuous contact with each other as they proceed upwards and downwards, respectively, through the packing.

Sensitivity studies characterizing column performance (i.e. temperature, component loadings, etc.) versus varying plant operating parameters (e.g. number of theoretical simulation trays, off-design flow/pressure/temperature/composition, etc.) are of paramount importance. This is especially true considering that CO_2 freezing (and approach to freezing) calculations are pressure, temperature, and composition dependent. These sensitivity studies can be used to explore and evaluate the widest operating regions to identify the most critical point(s) of concern.

Caveat: Column operations in most process simulators will allow the user to specify tray efficiencies so that an actual number of trays can be simulated. The simulators also allow the user to specify efficiencies for specific components for a particular column. The use of tray or component efficiencies in the column simulation can sometimes result in 1) non-equilibrium conditions (non-dew point tray vapors/non-bubble point tray liquids) or 2) dew point tray vapor/bubble point tray liquid streams where the individual, calculated phase temperatures do not match their respective stage temperatures. Since this introduces error, use of either of these efficiencies is not recommended when analyzing column CO_2 freezing. Simulation of theoretical trays is highly recommended for the prediction methods introduced here.

Tray Liquid Prediction

Liquid phase CO_2 freezing calculation procedures are the same for either packed or trayed columns. For each stage in the column, the temperature safety margin is calculated by comparing the stage temperature to the CO_2 freezing temperature predicted by an LSE calculation using either Eq. 1 or 2.

Tray Vapor Prediction

Vapor phase CO_2 freezing calculation procedures differ slightly depending upon whether a packed or a trayed column is being considered. For each stage in a packed column, the temperature safety margin is calculated by comparing the stage temperature to the CO_2 freezing temperature predicted by a VSE calculation using Eq. 4 and 5.

Vapor phase freezing in a packed column may be mitigated by washing of the solid CO_2 with the downflowing liquid. Determining the ultimate fate for this solid CO_2, once formed, is beyond the scope of this paper. The methods of this paper only show how to avoid situations in which solid will form in the first place.

The procedure for a trayed column follows in an analogous manner, however, the temperature safety margin for each stage is calculated by comparing the temperature of the tray above with the CO_2 freezing temperature predicted by a VSE calculation. Recall, that while the vapor is in equilibrium with its tray liquid, the vapor will contact the colder tray above. Any cooling of the vapor past its vapor-solid equilibrium point may result in desublimation of solid CO_2 onto the cold underside surface of the tray above. Weeping, frothing, entrainment, etc. may wash the solid CO_2 off of the bottom of the

tray above, but again analysis of the ultimate fate of the CO_2 and evaluating the potential for plugging in this situation is beyond the scope of this paper.

THE PROBLEM AT HAND

Our original column problem is a good example of how CO_2 concentration peaks can occur within a gas plant demethanizer under the right circumstances. As seen in Figure 6, particularly for the liquid phase, there is a concentration peak within the column due to carbon dioxide's relative volatility (to methane and ethane). This behavior is attributable to processing a unique gas composition at moderate ethane recovery levels. Note that steep changes in tray liquid CO_2 concentration are observed with modest changes in tray temperatures.

Having constructed the proper criterion and thermodynamic calculations for CO_2 freezing, we applied our prediction method to the simulation of this column. Our predicted freeze temperatures, as seen in Figures 6 and 7, indicated a severe problem with the proposed design. We acknowledge that the CO_2 freeze results from three process simulators, presented previously in Table I, qualitatively provide the same conclusion. However, for this particular case, it was necessary to change the process scheme and lower ethane recovery level in order to maintain reasonable CO_2 freezing margins. Reliance on the process simulators unreliable predictive capability was totally unacceptable. Achieving the highest ethane recovery without freezing was critical to the project's viability.

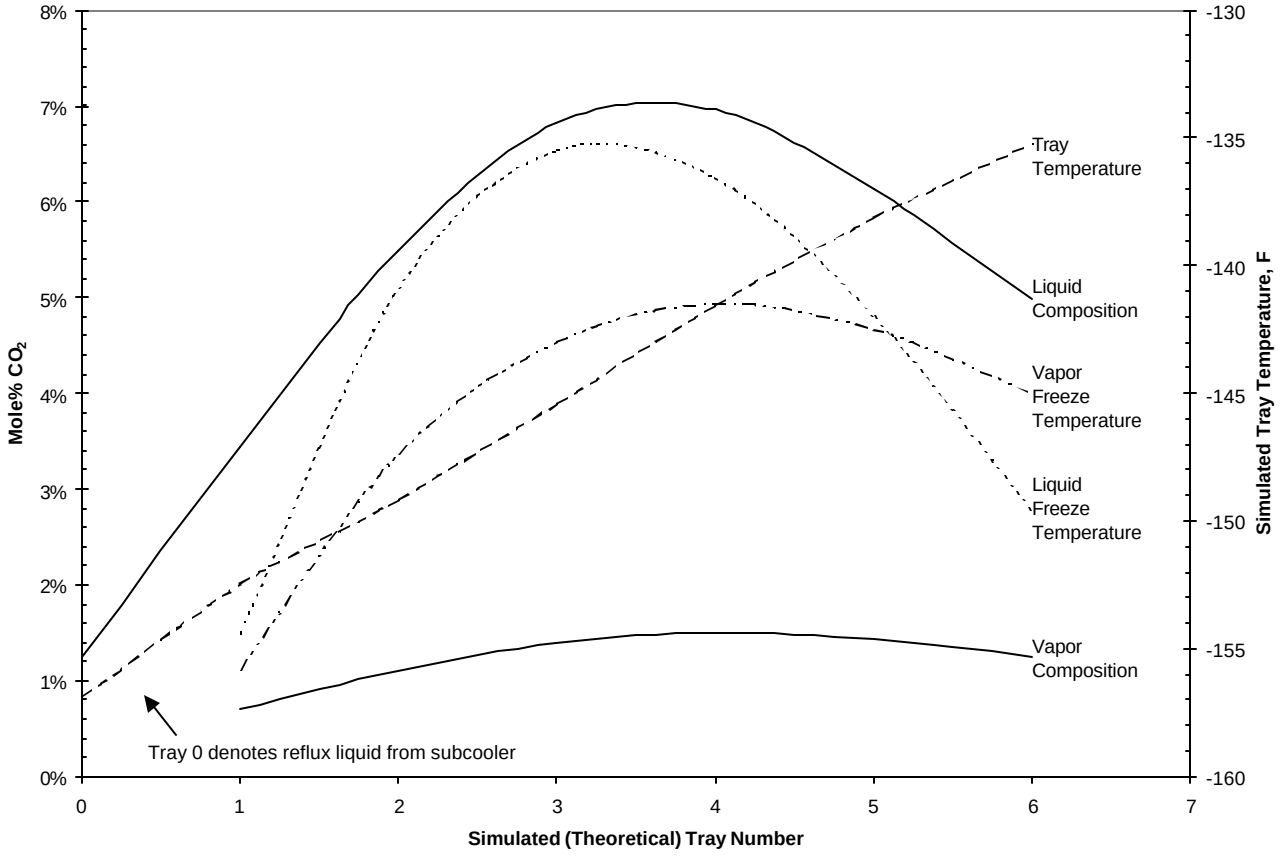


Figure 6 – Tray Profiles, Overhead Section of Demethanizer

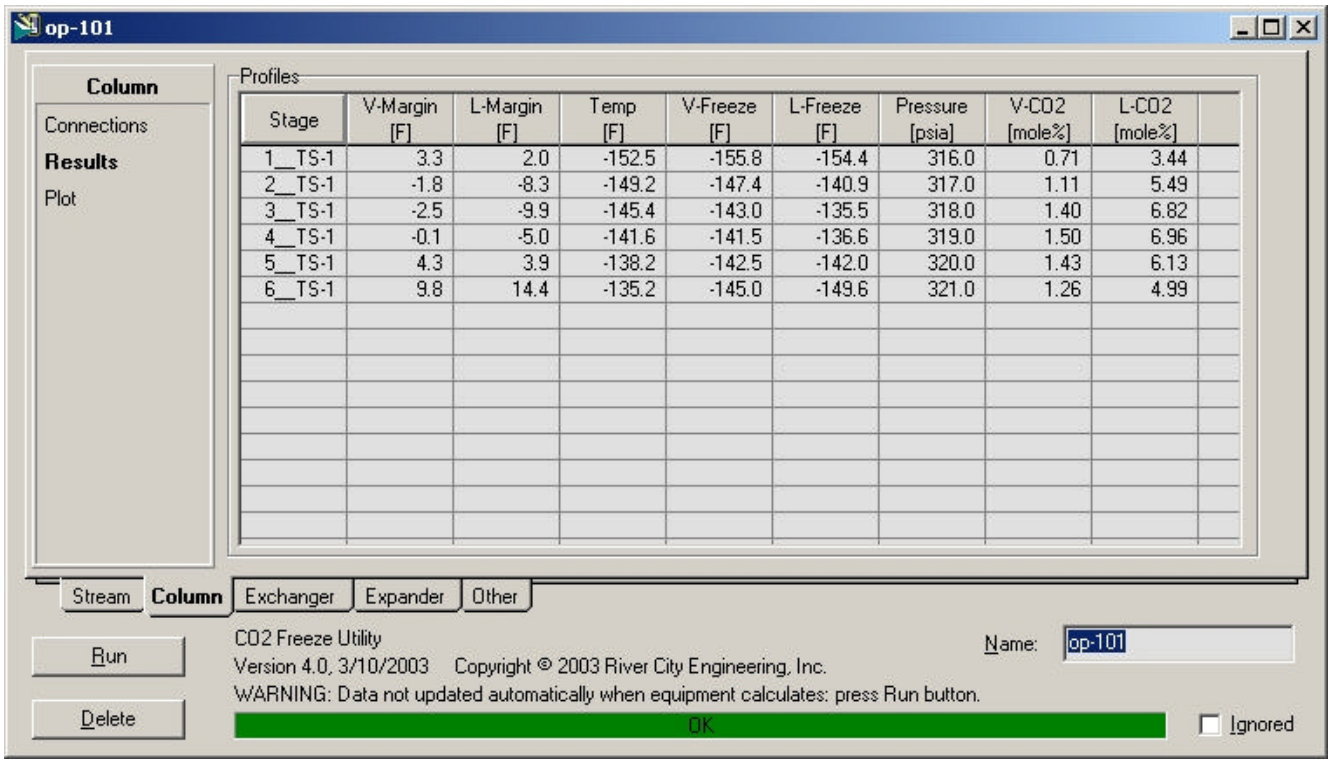


Figure 7 - CO_2 Freeze Predictions, Overhead Section of Demethanizer

The following are results of our VSE analysis for the off-design vapor stream previously shown in Table I:

Table III: Vapor CO_2 Freeze Comparison

Freeze Prediction-Simulator A	-190.3°F
Freeze Prediction-Simulator B	-190.2°F
Freeze Prediction-Simulator C	-190.3°F
GPSA: Figure 13-64	-155°F
This Work	**-146.5°F**

The lack of critically reviewed experimental vapor-solid data makes it difficult to judge which prediction is best. The predictions made by GPSA Figure 13-64 and by the methods of this paper qualitatively agree, while the predictions made by simulator A, B and C appear to be major outliers.

EXTENDING THE MODEL

To help verify our freezing predictions, we back-checked them against actual data from various operating plants. From these operating data, we have built simulation models for several different plants which have operated very near (or unfortunately at) their known CO_2 freezing points. These plants operate with widely varying gas richness and have ethane recovery levels in the range of 70-98%. The results of the comparison are shown in Table IV. The predicted freeze temperatures agree quite well with the observed plant freeze temperatures for all four facilities.

Table IV: Comparison of Actual Plant Freezing versus This Work

Plant #	Observed Plant Freeze Temperature*	**Predicted Freeze Temperature (this work)**	Absolute Δ	Limiting Freezing Criteria
1	-150.2°F	**-145.7°F**	4.5°F	LSE
2	-142.2°F	**-141.0°F**	1.2°F	VSE
3	-137.5°F	**-137.1°F**	0.4°F	VSE
4	-117.0°F	**-116.2°F**	0.8°F	LSE

* Simulated values reported

CONCLUSIONS

Unreliable predictions for the temperature of CO_2 freezing are being made by several of the commercial process simulators typically used by gas processors. Our need for dependable prediction sparked the review of existing experimental data, a review of the thermodynamics of solid formation, and the development of the calculation procedures presented in this paper.

Our thermodynamic models are capable of predicting the liquid-solid CO_2 freezing point for the methane-CO2 binary data in GPA RR-10 [2] to within ± 2.6 °F, but the uncertainty increases to ± 9.4 °F when considering data from additional sources. The accuracy of our models is far better than the accuracy of the commercial process simulators tested.

For the column problem presented here, it should be noted that Figure 13-64 of the GPSA Engineering Data Book [1] provides adequate liquid-solid CO_2 freezing prediction for the system in question. Tray liquid compositions closely approximate a methane-CO_2 binary system. Each are almost entirely comprised of methane, a small amount of ethane, and CO_2. Of course, this figure is built upon the underlying binary methane-CO2 freeze data which it represents. Its accuracy for other liquid systems with higher levels of non-methane and non-CO_2 components is expected to diminish.

The vapor-solid CO_2 freezing predictions made by GPSA Figure 13-64 and by the methods of this paper qualitatively agree. However, the lack of critically reviewed experimental vapor-solid data makes it difficult to judge which prediction is best. The accuracy of either appears far better than the accuracy of the commercial process simulators tested.

We have also presented procedures for analyzing CO_2 freezing in several common unit operations. Common pitfalls are avoided by carefully defining the temperature safety margin and by tailoring the thermodynamic calculations to the needs of the specific unit operation. We have incorporated these procedures into customized add-in extensions for commercial process simulators.

ACKNOWLEDGEMENTS

The authors would like to thank ConocoPhillips, without whom this work would not have been possible. We would also like to thank our colleagues at River City Engineering for comments, suggestions, data gathering, and data compilation during the development of this paper. Additional assistance was provided by Dan Hubbard of HPT, Inc. and Julie Howat of the University of Kansas (Kurata Thermodynamics Laboratory).

REFERENCES CITED

1. Engineering Data Book, Eleventh Edition, Gas Processors Suppliers Association, Tulsa, 1998.

2. Kurata, F., "Solubility of Solid Carbon Dioxide in Pure Light Hydrocarbons and Mixtures of Light Hydrocarbons", Research Report RR-10, Gas Processors Association, Tulsa, Feb. 1974.

3. Knapp, H., Teller, M., Langhorst, R., Solid-Liquid Equilibrium Data Collection: Binary Systems, Chemistry Data Series Vol. VIII, Part I, DECHEMA, 1987.

4. Davis, J.A., Rodewald, N., Kurata, F., "Solid-Liquid-Vapor Phase Behavior of the Methane-Carbon Dioxide System", AIChE J., Vol. 8, No. 4, p.537-539, 1962.

5. Brewer, J., Kurata, F., "Freezing Points of Binary Mixtures of Methane", AIChE J., Vol. 4, No. 3, p. 317-318, 1958.

6. Donnelly, H.G., Katz, D.L., "Phase Equilibria in the Carbon Dioxide-Methane System", Research Conference, Phase Behavior of the Hydrocarbons, University of Michigan, July 1&2, 1953.

7. Donnelly, H.G., Katz, D. L., "Phase Equilibria in the Carbon Dioxide-Methane System", Ind. Eng. Chem., Vol. 46, No. 3, p. 511-517, 1954.

8. Cheung, H., Zander, E.H., "Solubility of Carbon Dioxide and Hydrogen Sulfide in Liquid Hydrocarbons at Cryogenic Temperatures", Chem. Eng. Progr. Symp. Ser., Vol. 64, p. 34-43, 1968.

9. Mraw, S.C., Hwang, S.C.., Kobayashi, R., "Vapor-Liquid Equilibrium of the CH_4-CO_2 System at Low Temperatures", Jour. Chem. Eng. Data, Vol. 23, No. 2, p. 135-139, 1978.

10. Sterner, C.J., "Phase Equilibria in CO_2-Methane Systems", Adv. Cryog. Eng., Vol. 6, p. 467-474, 1961.

11. Jensen, R.H., Kurata, F., "Heterogeneous Phase Behavior of Solid Carbon Dioxide in Light Hydrocarbons at Cryogenic Temperatures", AIChE J., Vol. 17, No. 2, p. 357-364, March, 1971.

12. Clark, A.M., Din, F., "Equilibria Between Solid, Liquid and Gaseous Phases at Low Temperatures: The System Carbon Dioxide+Ethane+Ethylene", Disc. Faraday Society, Vol. 15, p. 202-207, 1953.

13. Im, U.K., Kurata, F., "Solubility of Carbon Dioxide in Mixed Paraffinic Hydrocarbon Solvents at Cryogenic Temperatures", Jour. Chem. Eng. Data, Vol. 17, No. 1, p. 68-71, 1972.

14. Pikaar, M.J., "A Study of Phase Equilibria in Hydrocarbon-CO_2 System", Ph.D. Thesis, University of London, London, England, October, 1959.

15. Din, F., Thermodynamic Functions of Gases, Vol. 1, Butterworths, London, 1962.

16. Im, U.K., "Solubility of Solid Carbon Dioxide in Certain Paraffinic Hydrocarbons: Binary, Ternary and Quaternary Systems", Ph.D. Thesis, University of Kansas, May, 1970.

17. Renon, H., Prausnitz, J.M., AIChE J. Vol. 14, No. 1, p. 135-144, January, 1968.

18. Peng, D.Y., Robinson, D.B., "A New Two-Constant Equation of State", Ind. Eng. Chem. Fund., Vol. 15, No. 1, 1976.

19. Peng, D.Y., Robinson, D.B., "Calculation of Three-Phase Solid-Liquid-Vapor Equilibrium Using an Equation of State", p. 185-195, in Chao, K.C., Robinson, R.L., (editors), "Equations of State in Engineering and Research", Advances in Chemistry Series 182, American Chemical Society, Washington, DC., 1979

20. Zhi, Y., Lee, H., "Fallibility of Analytical Roots of Cubic Equations of State in Low Temperature Region", Fluid Phase Equilibria, Vol. 201, p. 287-294, 2002.

21. Press, W.H., Vetterling, W.T., Teukolsky, S.A., Flannery, B.P., Numerical Recipes in FORTRAN 77: The Art of Scientific Computing, 2nd Ed., Vol. 1, Cambridge University Press, 1992.

22. Poling, B.E., Grens II, E.A., Prausnitz, J.M., "Thermodynamic Properties from a Cubic Equation of State: Avoiding Trivial Roots and Spurious Derivatives", Ind. Eng. Chem. Proc. Des. Dev., Vol. 20, p. 127-130, 1981.