

# **RETROGRADE PHENOMENA IN FLUID PHASE EQUILIBRIA**

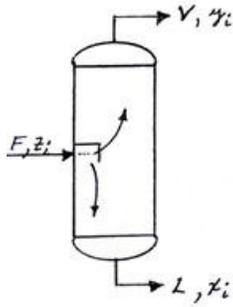
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## RETROGRADE PHENOMENA IN FLUID PHASE EQUILIBRIA



Occasionally the occurrence of retrograde condensation phenomena is encountered in the design of refineries and gas processing plants. In this paper, we analyze retrograde phenomena in a typical natural gas mixture and then specifically address the occurrence of this phenomenon in hydrogen-containing systems. It will be demonstrated that a very small change in the concentration of hydrogen can have a dramatic effect on the shape and location of the P-T phase envelope, especially on the bubble point locus.

In light of the above analyses, we then provide an explanation to the observations made for two case histories reported for a naphtha unifier reactor effluent stream and a high pressure bottoms liquid stream involved in a hydro-desulfurizing unit. Both cases histories studied here involve petroleum fraction-rich streams containing a rather small concentration of hydrogen.

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## RETROGRADE PHENOMENA IN FLUID PHASE EQUILIBRIA

**Introduction** Occasionally the occurrence of retrograde condensation phenomena is predicted in the design of refineries and petrochemical processing plants. Two typical case histories, one being anonymous, are described below.

In the first instance, process engineers from a major engineering and construction company encountered this phenomenon in the design of a naphtha unifier reactor. The composition breakdown of the reactor effluent, which contained hydrogen and a host of other hydrocarbons and petroleum cuts, is given in the upper portion of Table 1. Using a process simulator and a sound VLE correlation these engineers proceeded to flash the effluent stream at 540 psia over the temperature range 0 to 600 deg. F. The results are listed in the lower portion of Table 1. A bubble point is indicated at about 102 deg. F. As the temperature is lowered (isobarically) from this point, the quantity of vapor increased. At temperatures higher than the apparent bubble point, no vapor formation was indicated.

In another case, cited by Adler et. al. (1), a hydrodesulfurization unit was being designed. A process engineer performed a computer calculation involving heating of a bubble point liquid (the bottom of a high pressure separator) from 110 deg. F to about 600 deg. F at a design pressure of 940 psia. The stream was then subsequently fed to an H<sub>2</sub>S stripping column. The computer output indicated that the stream was all liquid. Even though it was at its bubble point initially and was then heated to nearly a 500 deg. F higher temperature, it was still liquid. The composition of the bubble point liquid is given in Table 2. The mixture consists of more than 80 mole percent heavy oils. However, the presence of the light components, especially hydrogen, still strongly influence mixture behavior. Later it will be demonstrated that a very small amount of hydrogen can have a large effect on the shape of the phase envelope, especially the bubble point locus.

In the ensuing discussions we will study retrograde behavior in a typical natural gas mixture and then specifically address the occurrence of this phenomenon in hydrogen-containing systems.

**Typical P-T Diagram** Figure 1 is a typical P-T diagram for a relatively close-boiling paraffin-paraffin mixture. Let us first consider traverse A-B. By starting at A (all liquid stream) and increasing the temperature at constant pressure, we first contact the bubble point curve. At this point vapor begins to form. An increase in temperature causes more vaporization. At still higher temperatures, the quantity of vapor then begins to decrease until the mixture becomes all liquid once again at Point B, a second bubble point temperature.

This phenomenon is commonly referred to as isobaric retrograde condensation.

A similar phenomenon is shown by Traverse D-C where, at constant temperature, the dew point curve is cut twice. If the pressure is lowered isothermally from Point D,

the dew point curve will eventually be met i.e. the mixture is all vapor (saturated). Upon lowering the pressure even further, we then note that the quantity of liquid begins to increase. At still lower pressures, the system begins to behave as normally expected, and vaporization becomes more prominent until a second dew point (Point C) is reached. In other words, several quality (% vapor) curves are cut twice during the traverse.

**Natural Gas Mixture** In order to study retrograde behavior, we require a robust VLE correlation that can reasonably be applied in the critical region of pure components and mixtures. Such a predictive correlation is based on the two-constant Peng-Robinson (PR) cubic equation of state (2). This equation incorporates the best features of the Soave modification (3) of the original Redlich-Kwong equation (4) into an improved model which has significant advantages over these two earlier two-parameter equations of state. Some of these improved features are:

1. Superior performance in the vicinity of the critical point and throughout the upper retrograde region,
2. Superior prediction of liquid densities.
3. The PR equation predicts a more realistic universal critical compressibility factor of 0.307, whereas the RK and Soave equations each predict a  $Z_c$  value of 0.333.

We have used the process simulator PROVISION (Program PROII developed by Simulation Sciences, Inc.) with the Peng-Robinson thermodynamics option to study the behavior of a typical natural gas mixture in the retrograde region. This natural gas mixture was one of several studied experimentally by Yarborough (5) and also used by Peng and Robinson (2) to develop and test their equation of state. The phase envelope generator from PROVISION was then used to generate the P-T diagram depicted in Figure 2 for this natural gas mixture.

Also plotted on this phase boundary are the critical point C, cricondenbar CB and the cricondentherm CT. A complete definition of these terms is given in Table 3. The critical point is situated in such a way that the retrograde region basically involves the dew curve only. We performed a series of isothermal-isobaric flash calculations, first along the 200 deg. F isotherm and then along the 3200 psia isobar. In either case, the dew curve can be cut twice.

Figure 3 shows the calculated flash liquid history for each of these traverses. In each case the liquid fraction (liquid mole percent) goes through a maximum, thus verifying that we are operating in the retrograde region. Figure 4 shows the behavior of the individual component vapor-liquid equilibrium ratios when plotted against pressure

for the 200 deg. F isotherm. An "approximate" convergence pressure ( $P_g$ ) of about 3300 psia is indicated where all equilibrium ratios appear to converge to a value of unity. It should also be noted here that the predicted equilibrium ratios agree quite nicely with Yarborough's experimental values.

**Hydrogen-Naphtha Kay** (6) has measured experimental bubble/dew point data for three hydrogen-naphtha mixtures. Figure 5 shows the results for 2.7, 5.2 and 9.8 mole percent hydrogen plotted in terms of P versus T diagrams. The naphtha is comprised of a narrow boiling fraction composed principally of pentanes and hexanes. By observing the set of bubble curves, we see that as we lower the temperature isobarically, the concentration of hydrogen in the liquid decreases. These data demonstrate the so-called "reverse" solubility effect of hydrogen. The explanation for this behavior is that such systems, which are inherently wide-boiling, are in a region of isobaric retrograde condensation.

Kay's data reveal a minimum in the bubble point locus for 2.7 and 5.2 mole percent hydrogen. For the 9.8 percent mixture no minimum occurs in the bubble curve. In the latter case, the bubble curve rises rather sharply at lower temperatures. The dew curves for all the mixtures appear to behave in the normal expected manner.

Kay postulates that the complete P-T diagram for a hydrogen-naphtha mixture having a minimum in its bubble point curve might appear something like that shown in Figure 6. Based on Kay's results for 9.8 mole percent hydrogen in naphtha, Figure 7 could also describe the P-T behavior when no minimum occurs in the bubble point locus. At pressures in proximity of the critical point, isobaric retrograde condensation can definitely take place. At fixed pressure, the bubble point curve will be intersected at least twice and, on rare occasion, maybe as many as four times. Due to the rather wide-boiling nature of these systems, a broad range in pressure and temperature exists over which isobaric retrograde condensation can occur.

**Hydrogen-n-Hexane** To further illustrate retrograde behavior in wide-boiling systems, the binary system hydrogen-n-hexane was studied in some detail.

Using the process simulator PROVISION with the Peng-Robinson thermodynamics option, we generated three P-T phase envelopes for 2, 4 and 10 mole percent hydrogen in n-hexane. In the qualitative sense, it turns out that the predicted phase boundaries behave in a very similar manner as do the hydrogen-naphtha phase boundaries measured and reported by Kay. Figures 8 and 9 cover 2 and 4 mole percent hydrogen in n-hexane and display characteristic minima in their respective bubble point curves. Figure 11 is the predicted phase boundary plot for 10 mole percent hydrogen in n-hexane. In this case, the minimum in the bubble curve has vanished.

We performed a series of isoflashes at fixed P and T along the 440 psia isobar for 4 mole percent hydrogen in hexane using the PR equation. In Figure 9 we show that the PR predicted bubble curve is cut twice and the dew curve once. Figure 10 shows the predicted flash vapor history for this isobar plotted against temperature. Starting at 25 deg. F and increasing the temperature until the first bubble point (about 150 deg. F) is reached, we see that the quantity of vapor steadily decreases to zero. Between 150 deg. F and about 400 deg. F (second bubble point), the system is all liquid. Above 400 deg. F the amount of vapor begins to increase with increasing temperature as would normally be expected. Finally, the dew temperature (about 450 deg. F) is reached, and the system resides totally in the vapor state.

In Figures 8, 9 and 11 we have plotted the bubble and dew point loci calculated from the experimental measurements of Nichols et. al. (7). The experimental bubble loci lie well above the bubble loci predicted by the PR equation. However, the dew point loci show excellent agreement. This is not surprising, because all of the dew point loci fall very close to the vapor pressure P-T curve for pure n-hexane.

The three bubble point loci for hydrogen-n-hexane were next calculated using the Chao-Seader correlation (8) and the modified van der Waals equation developed by Koppány (9). These latter two predicted loci tended to agree more closely with the bubble point loci measured by Nichols and also lie significantly higher than the PR predicted bubble loci. These comparisons are also included on Figures 8, 9 and 11.

As a final observation here, we see that the 440 psia isobar, which cuts the PR predicted bubble point curve of Figure 9 twice, lies well below the bubble point curves measured by Nichols or calculated by the Chao-Seader and Modified VDW correlations. This result means that at 440 psia the latter measured and predicted bubble curves are not intersected at all, and only the dew curve(s) will be cut once. This comparison clearly demonstrates the great sensitivity of the bubble point pressure to the low concentration of the light (very volatile) component in the liquid phase.

**Ternary Mixture** Figure 12 shows the P-T phase boundaries for two ternary mixtures containing H<sub>2</sub>-N<sub>2</sub>-CH<sub>4</sub> that were predicted by the modified van der Waals equation. In both mixtures, the relative amount of nitrogen and methane are the same. However, the hydrogen concentration is increased from about 2 mole percent to about 4 mole percent. This fairly small increase in hydrogen content has a very significant effect on the bubble point pressure at any particular temperature. For instance, at - 240 deg. F, this 2 mole percent increase in hydrogen content causes the bubble point pressure to increase by 330 psi. In either case, the predicted dew point curves are nearly identical except in the region of the critical point (estimated).

**Two Case Histories** In light of the discussions we have just completed, we can now offer an explanation to the observations made for the two cases history studies cited in the Introduction to this paper. In either case, the initial stream condition consists of a bubble point condition as described below:

<u>Case History</u>	<u>Mole % H<sub>2</sub> in the HC-rich mix</u>	<u>Bubble Pt. Condition</u>	
		<u>Press., Psia</u>	<u>Temp., F</u>
1	1.5	540	102
2	3.2	940	110

Figure 13 shows two qualitative sketches for the P-T phase boundaries that are believed to exist for these two streams. In either case, the stream is being processed in the isobaric retrograde region. Starting at the bubble point condition, as the temperature is increased at fixed pressure, no vaporization takes place until a second bubble point at a significantly higher temperature level is reached. If the temperature is decreased below the bubble point, then the extent of vaporization will become greater, as is clearly shown on either sketch of Figure 13.

To truly verify these observations, we would need to run (simulate) the two mixtures described in Tables 1 and 2 on a computer simulator using a sound thermodynamic VLE option. To do this, we require at least one more property other than the NBP to characterize each petroleum cut. This additional property could consist of the API liquid gravity or the Watson Characterization Factor,  $K_w$ .

### List of References

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9. Koppány, C.R., "Improved Predictions of Liquid Specific Volumes and Thermodynamic Properties From Two Separate Modifications of the van der Waals Equation", Parts 1-4, (2010-2011). Refer to the web site: [CRKTECH.COM](http://CRKTECH.COM).

**Table 1****Retrograde Behavior of a Naphtha Unifiner Reactor Effluent**

## A. Composition of the Effluent

<u>Component</u>	<u>Mole Percent</u>
Hydrogen	1.53
Ammonia	0.03
Hydrogen Sulfide	0.49
Water	0.01
Methane	2.78
Ethane	1.48
Propane	0.97
Isobutane	0.18
n-Butane	0.35
Isopentane	0.09
n-Pentane	0.30
125 F Avg BP	6.02
140 F Avg BP	0.00
175 F Avg BP	9.94
225 F Avg BP	16.40
275 F Avg BP	21.44
325 F Avg BP	20.24
375 F Avg BP	14.09
415 F Avg BP	<u>3.67</u>
	100.01

Total lb-moles of Effluent = 19,912.20

**Table 1 Continued**

## B. Flash Results (Unifiner Reactor Effluent) at 540 Psia

<u>Flash Temperature Deg. F</u>	<u>Lbmoles of Vapor Formed</u>
600	0
500	0
400	0
300	0
200	0
150	0
120	0
110	0
105	0
≅ 102	0 (BP)
100	0.6
95	6.6
90	12.5
70	31.7
50	40.9
0	81.6

**Table 2****Retrograde Behavior of a Hydrodesulfurizer  
High Pressure Separator Liquid**

<u>Component</u>	<u>Mole Percent</u>
Hydrogen	3.2
Hydrogen Sulfide	5.6
Methane	4.62
Ethane	0.47
Propane	0.57
Butane	0.46
100 F Avg BP	0.05
155 F Avg BP	0.28
245 F Avg BP	0.54
300 F Avg BP	0.36
345 F Avg BP	0.37
460 F Avg BP	6.34
565 F Avg BP	12.50
645 F Avg BP	16.28
705 F Avg BP	16.37
760 F Avg BP	15.04
805 F Avg BP	9.82
855 F Avg BP	<u>7.14</u>
	100.01

**Table 3****Definition of Key Points Located on a P-T Phase Boundary**

(See Figure 2)

**CRITICAL POINT** For mixtures this point is not, in general, the highest pressure and temperature at which two phases can coexist. Rather this is the point on the two-phase locus at which the properties (density for example) of the liquid and vapor become identical. It is also the point at which all constant quality lines (percent vapor) converge.

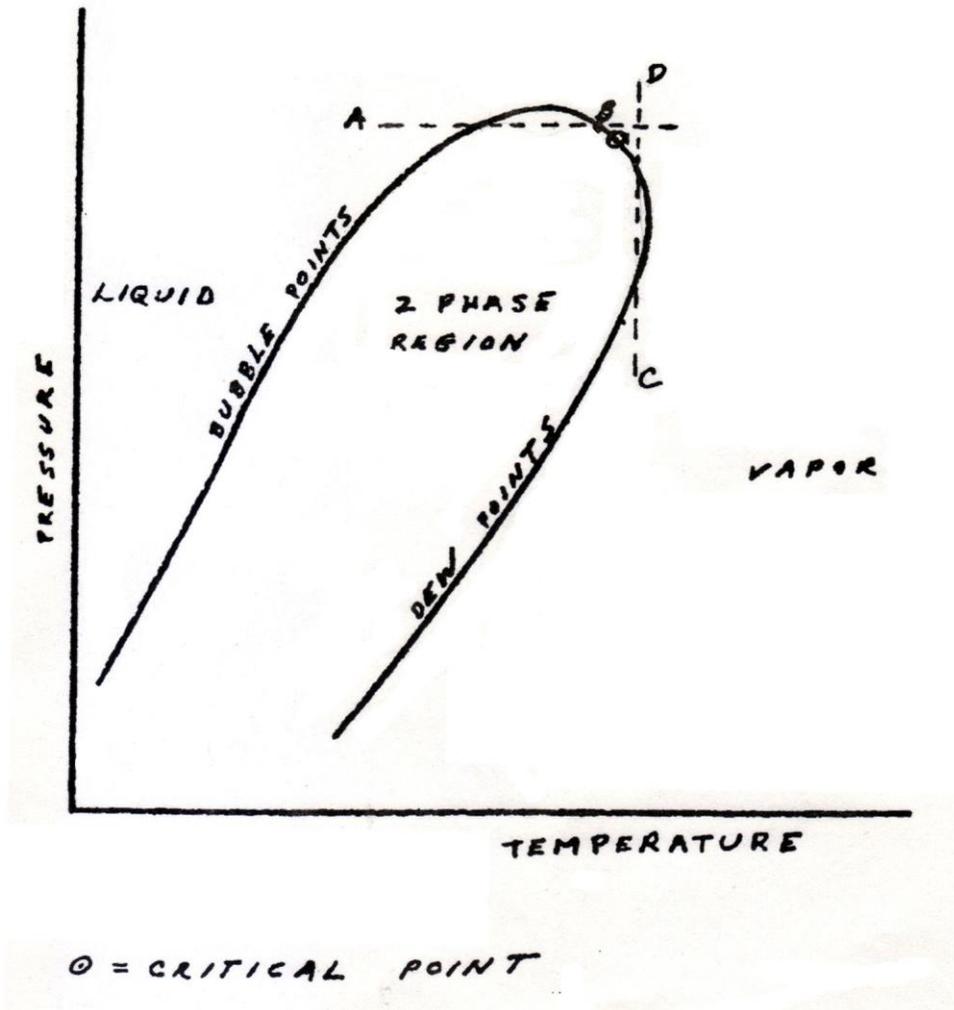
**CRICONDENBAR** For mixtures this point is the highest possible pressure at which two phases (liquid and vapor) can coexist.

**CRICONDENTHERM** For mixtures this point is the highest possible temperature at which two phases (liquid and vapor) can coexist.

**PURE COMPONENT** For a pure component all of the points described above coincide and become equal.

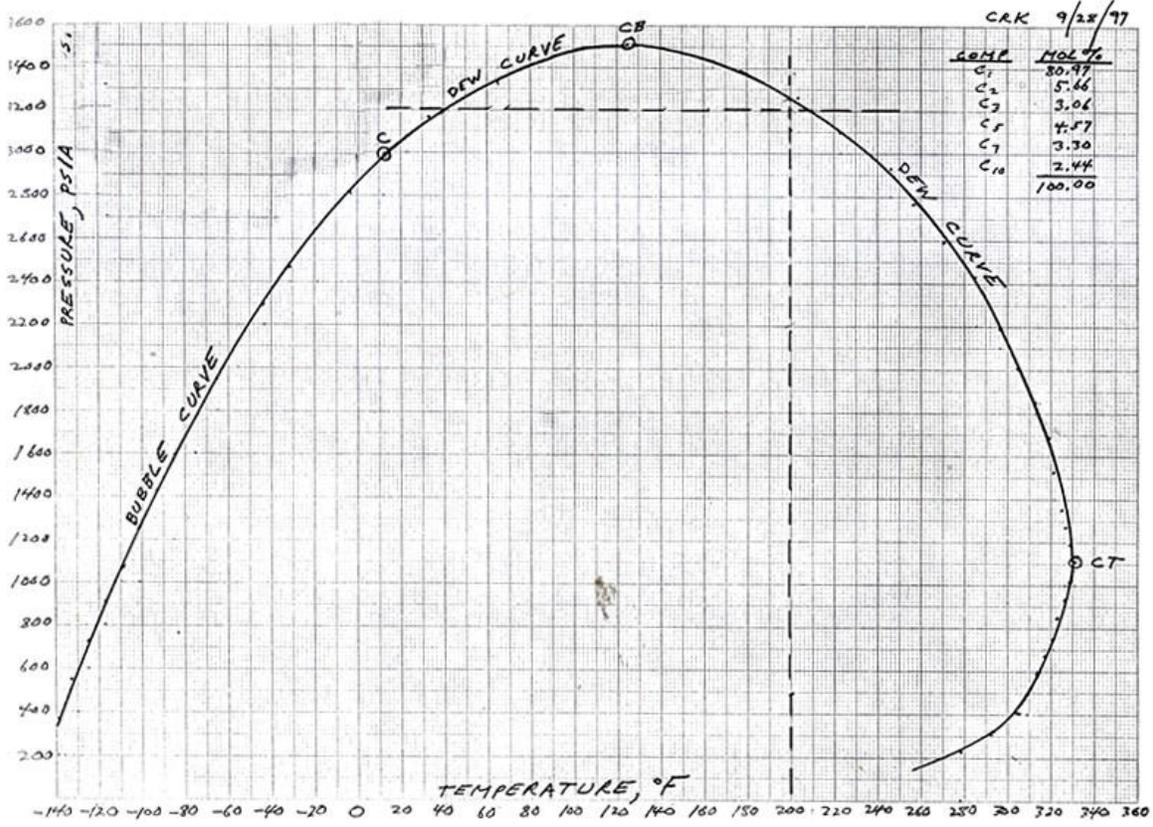
**Figure 1**

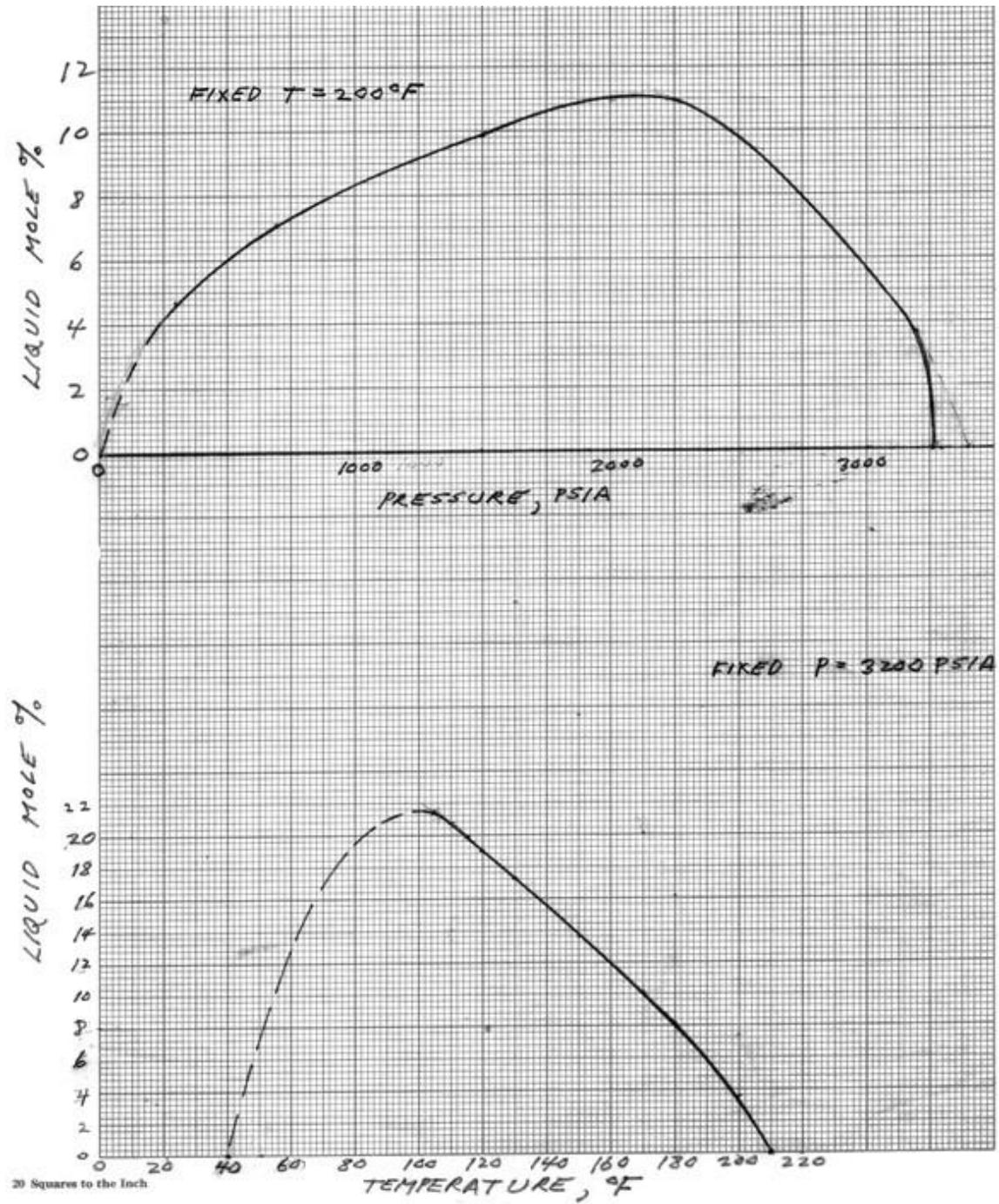
**Typical P-T Diagram For A Binary System**  
(e.g. Simple Paraffin-Paraffin Mixture)



**Figure 2**

**P-T Phase Envelope For A Natural Gas Mixture**



**Figure 3****Flash Liquid History In The Retrograde Region  
Of A Natural Gas Mixture**

**Figure 4**

**Vapor-Liquid Equilibrium Ratios For A Natural Gas at 200°F In The Retrograde Region**

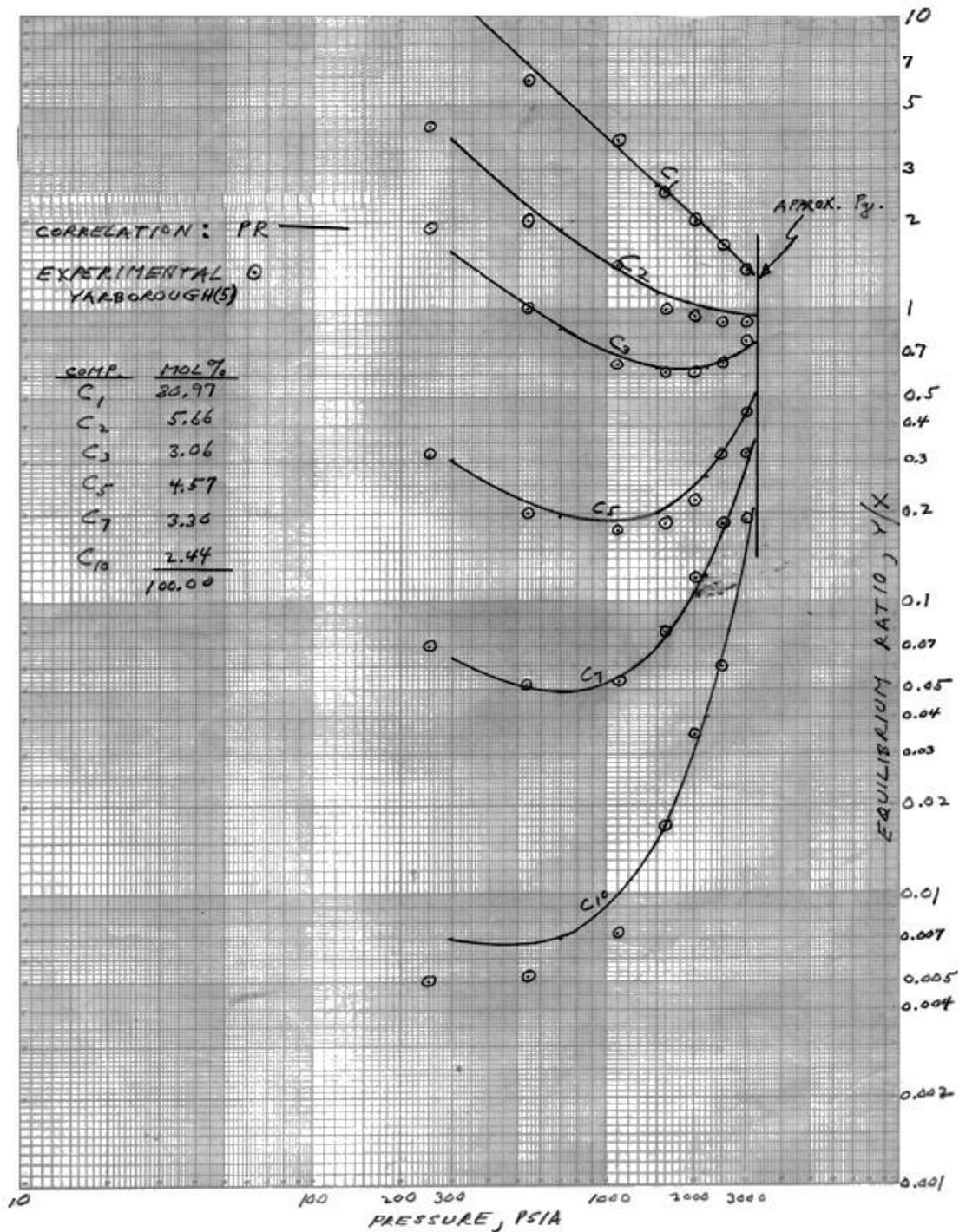
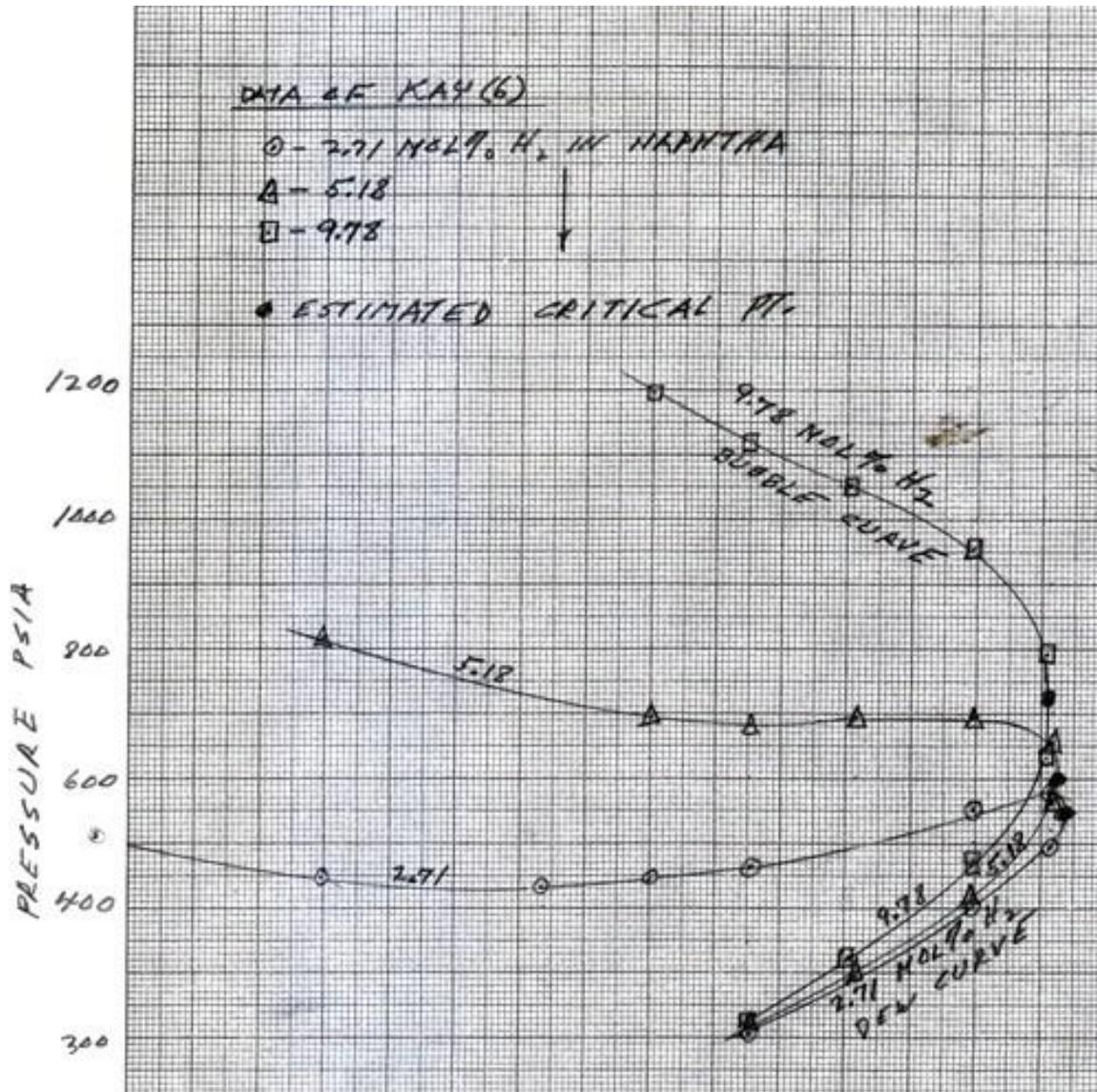
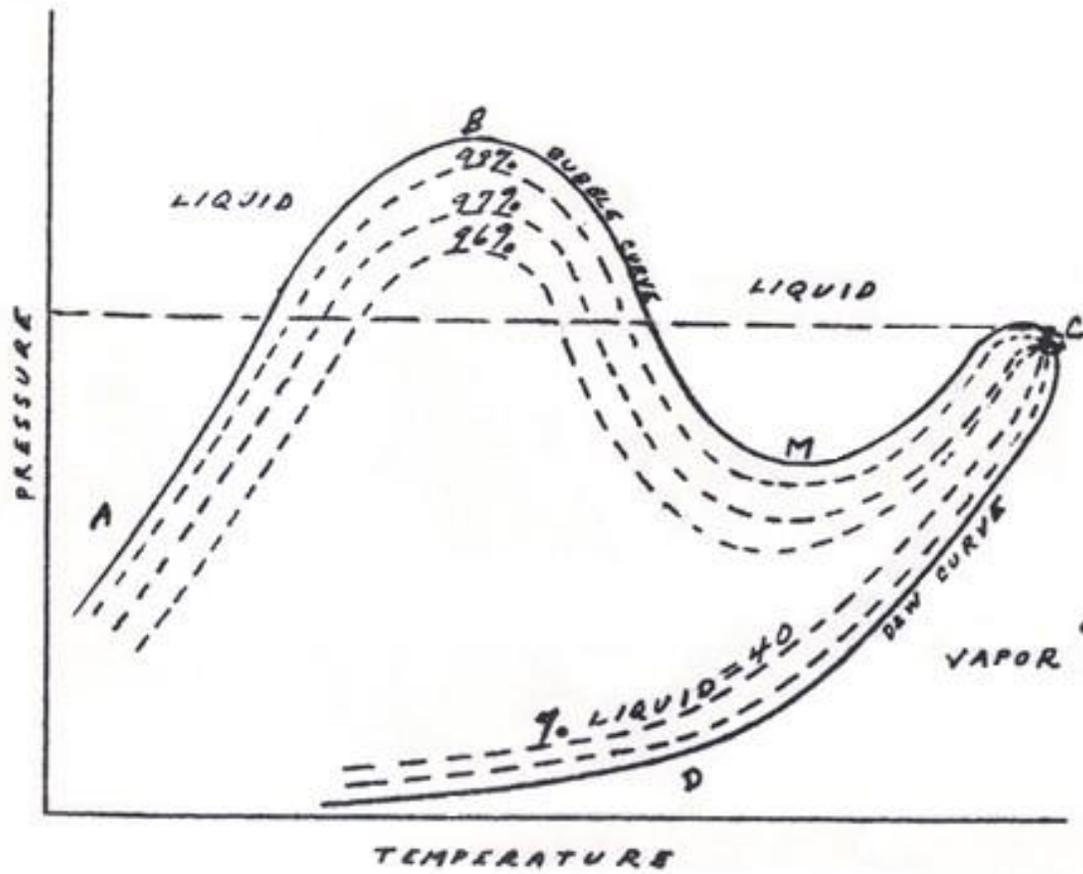


Figure 5

P-T Bubble-Dew Curves For Three H<sub>2</sub>-Naphtha Mixtures

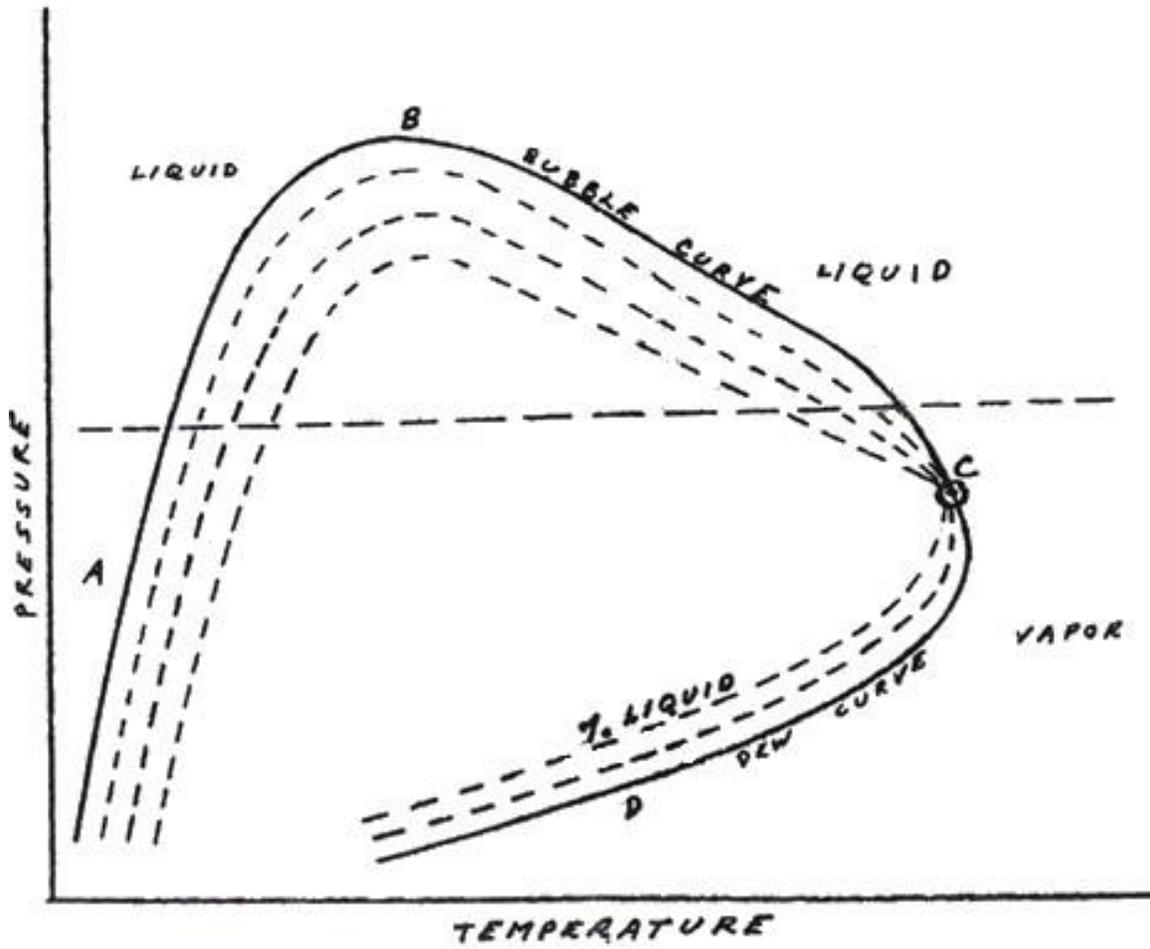
**Figure 6**

**P-T Diagram Showing Kay's Estimated Behavior Of  
Hydrogen-Naphtha Systems (Effective Binary With H<sub>2</sub>  
As The Light Component**



**Figure 7**

Alternative P-T Diagram For H<sub>2</sub>-Naphtha Or H<sub>2</sub> Containing Systems In General



⊙ = CRITICAL POINT

Figure 8

P-T Loci For 2 Mole % H<sub>2</sub> In  
n-Hexane

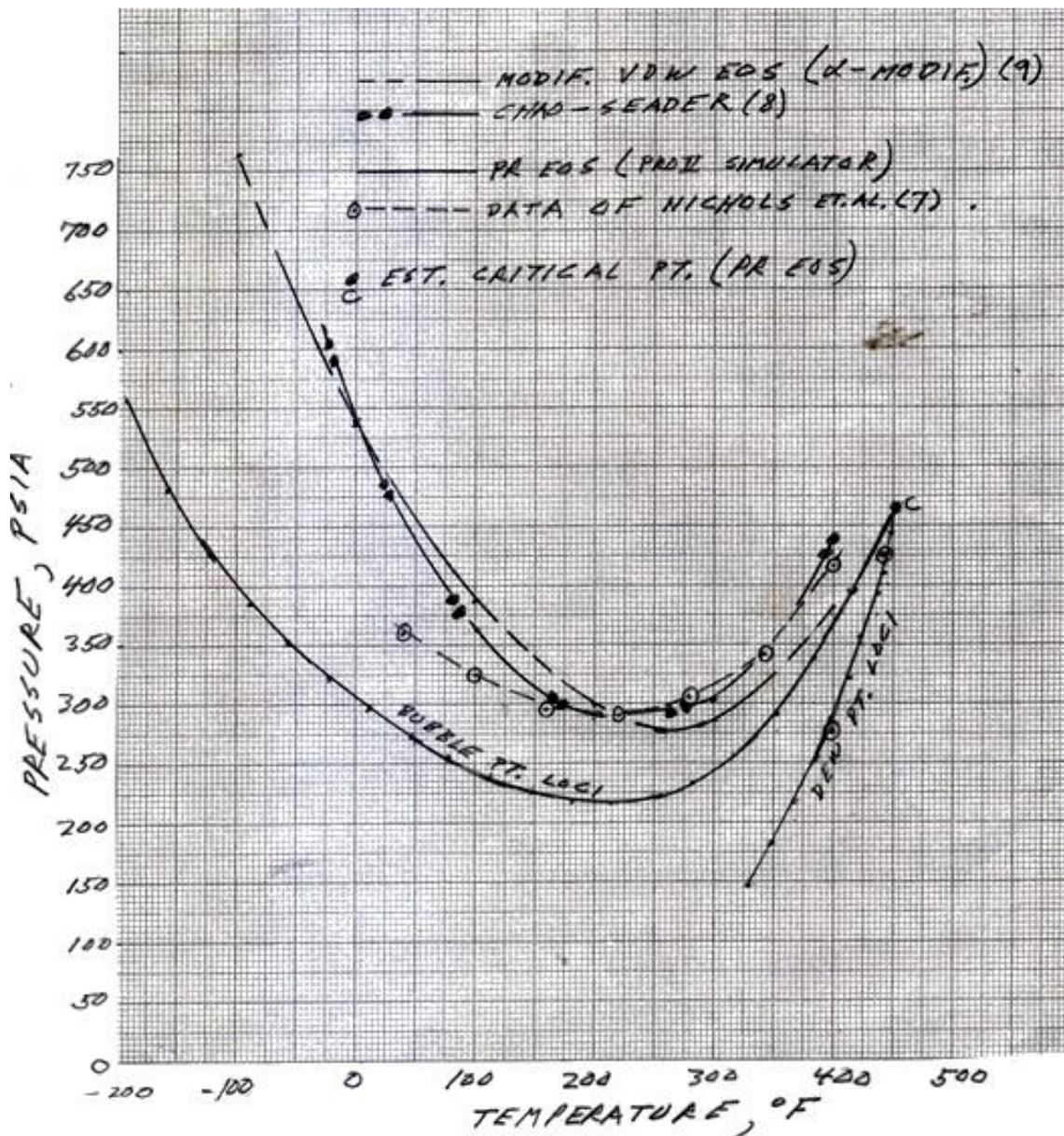
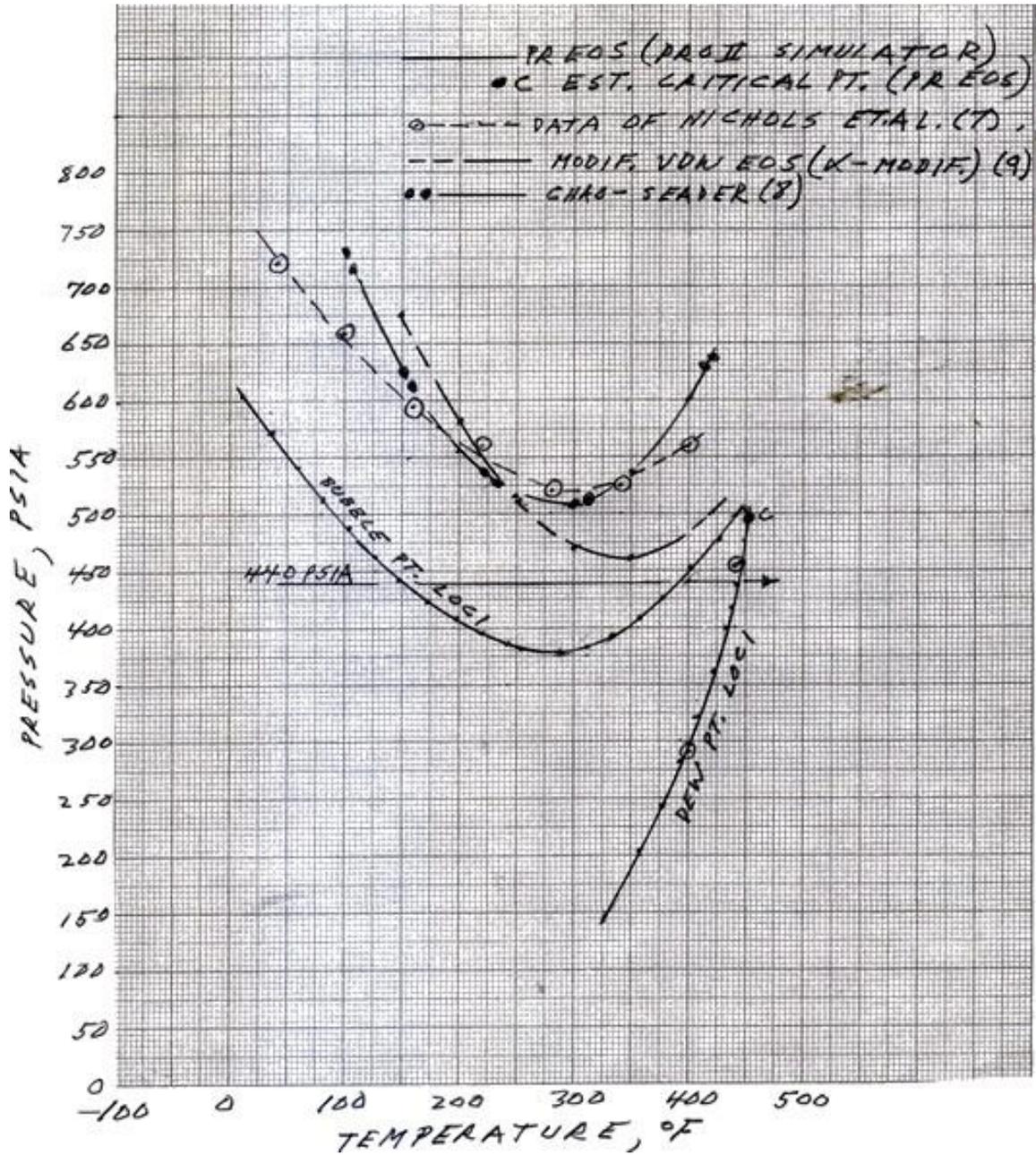


Figure 9

P-T Loci For 4 Mole % H<sub>2</sub> In  
n-Hexane



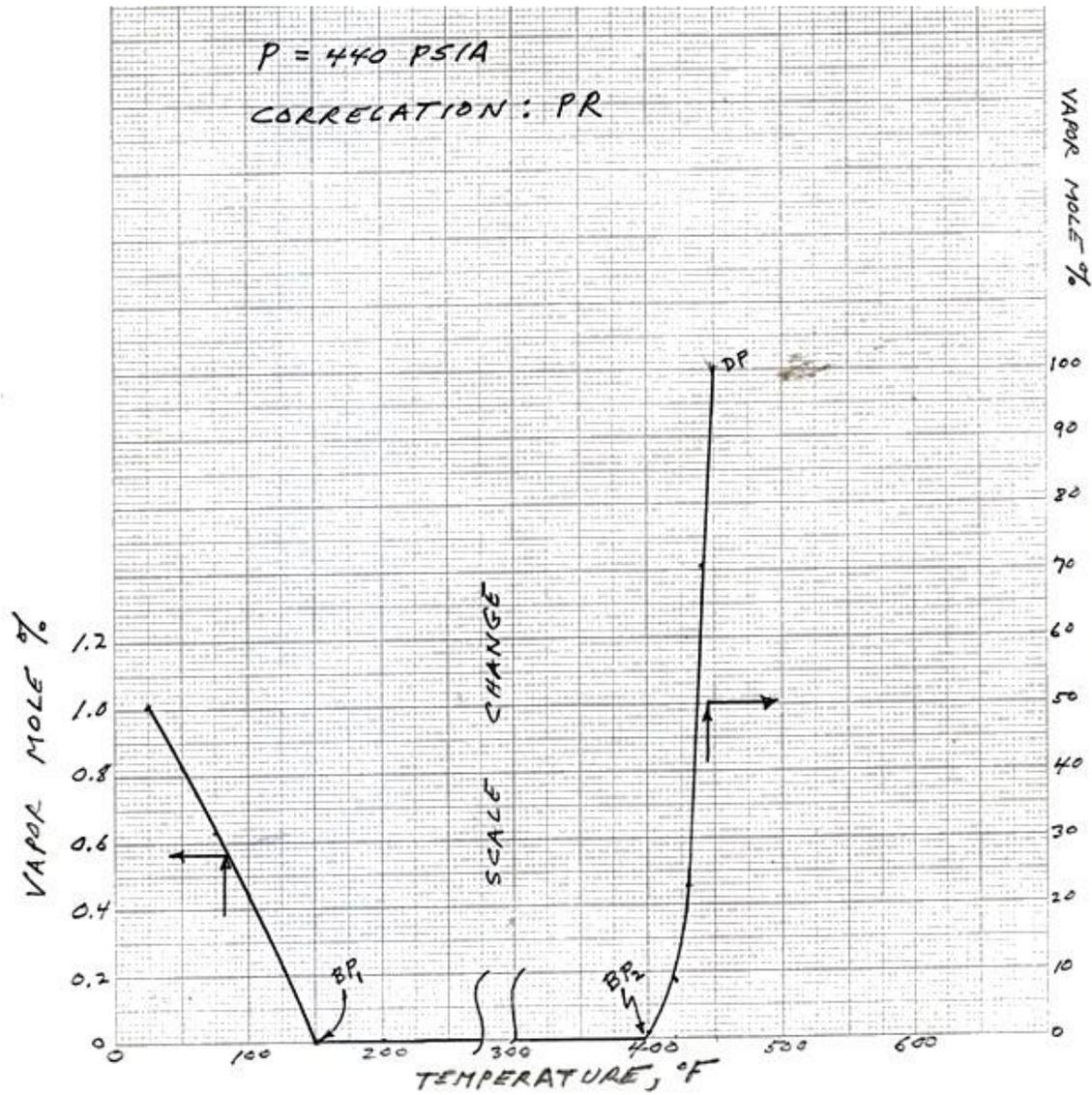
**Figure 10****Flash Vapor History In The  
Retrograde Region For 4 Mole %  
H<sub>2</sub> In n-Hexane**

Figure 11

P-T Loci For 10 Mole % H<sub>2</sub> In  
n-Hexane

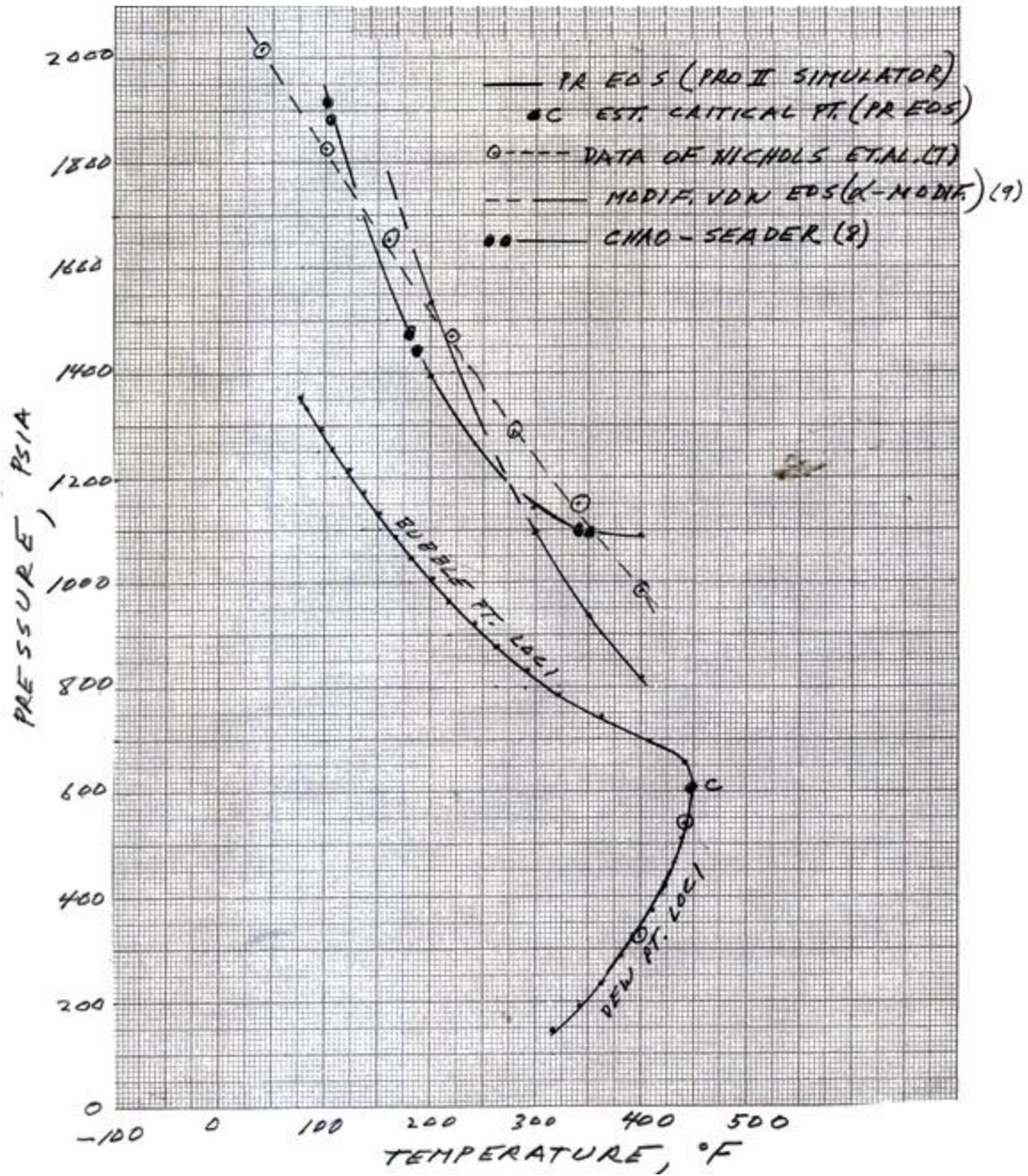
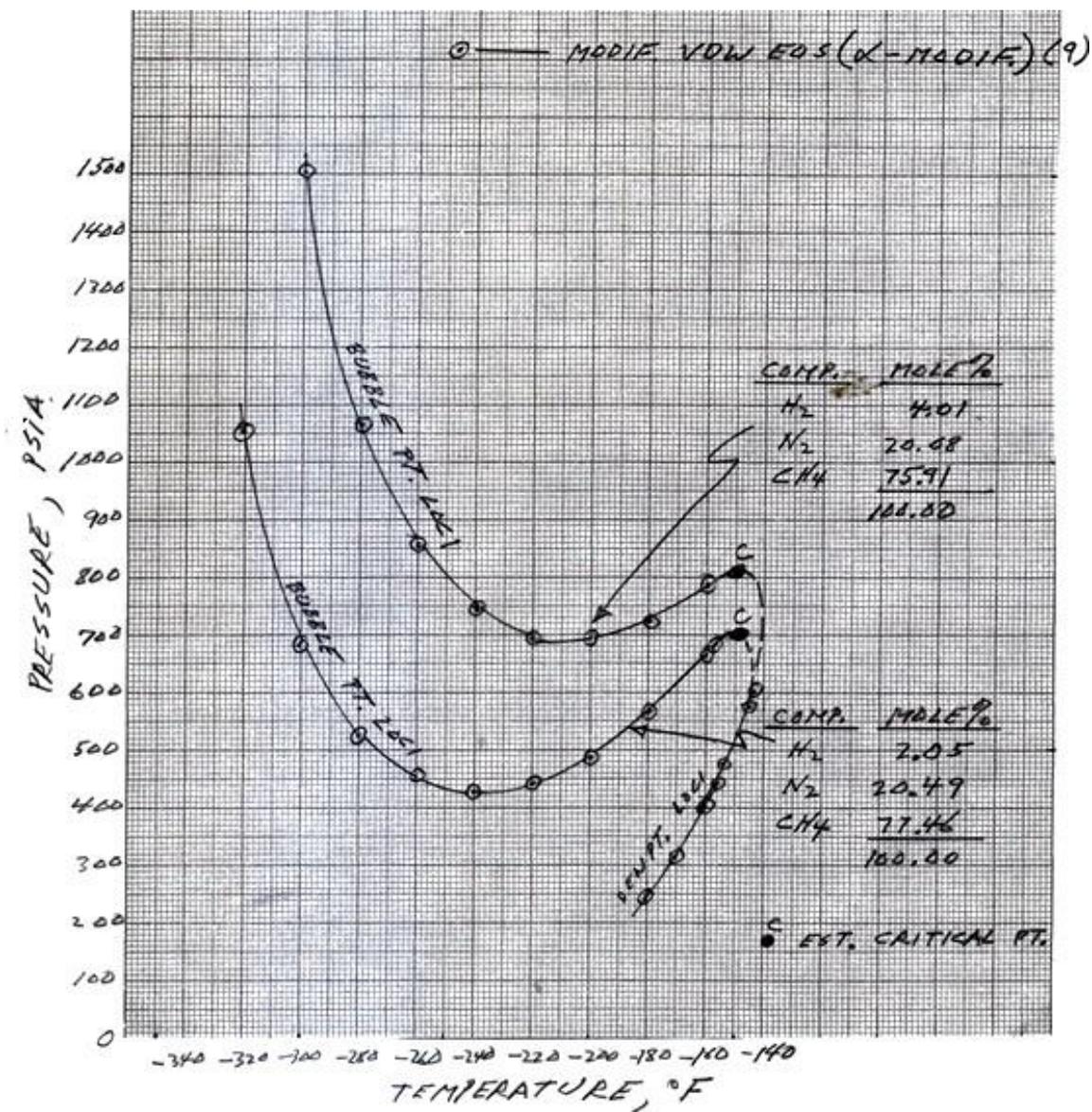


Figure 12

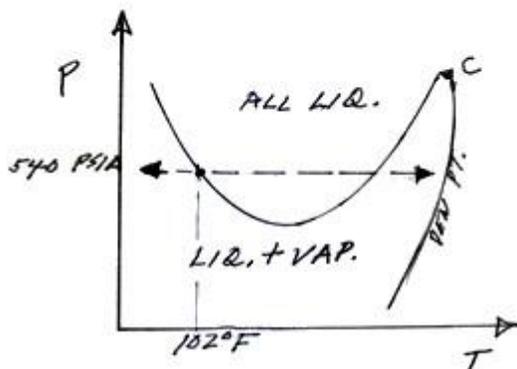
P-T Loci For Ternary  
Mixtures of H<sub>2</sub>/N<sub>2</sub>/CH<sub>4</sub>



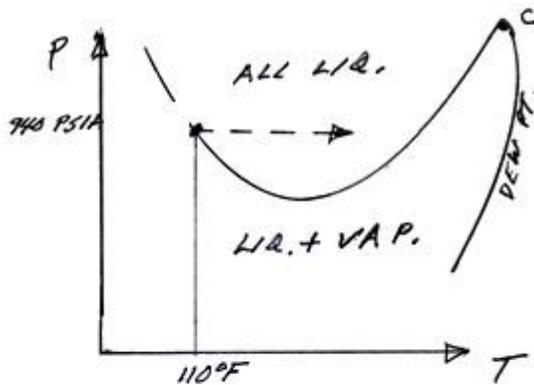
**Figure 13**

**Analysis Of Two Case  
Histories That Exhibit  
Retrograde Condensation  
Phenomenon**

I. CASE HISTORY NO. 1 (UNIFORMER REACTOR EFFLUENT)



II. CASE HISTORY NO. 2 (HIGH PRESS. SEPARATOR BTMS.)



● C CRITICAL PT.