RETROGRADE CONDENSATION

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The term "retrograde condensation" was first used by Kuenen at Leiden in 1892 to describe the behavior of a binary mixture during isothermal compression above the critical temperature of the mixture. Neither the contemporaries of Kuenen nor the recent investigators of the petroleum hydrocarbons have been consistent with Kuenen or with one another in the exact interpretation of the term. The phase behavior of simple and complex systems may be adequately described without the use of the term "retrograde condensation". The paper presents the phase behavior of simple and complex substances, including laboratory results on the phase relations of a mixture of natural gas and natural gasoline. The development of the concepts of vapor-liquid equilibria indicates that much of the phase behavior observed by the early investigators has not been utilized in present-day developments. The use of the term "retrograde condensation" is discussed; simple rules for nomenclature are recommended, which indicate that phase behavior may be adequately and probably more accurately described without the use of the term.

THE term "retrograde condensation" was first used by Kuenen at Leiden in 1892 (29). He was conducting experimental work on the phase behavior of a binary mixture to prove the theoretical deductions he had made, which were based on van der Waal's theory (51). During compression of this binary mixture at a temperature above the critical temperature of the mixture, Kuenen observed the formation of liquid followed by vaporization of the liquid with further pressure increase. This phenomenon Kuenen called "retrograde condensation".

The theory of van der Waal's (51) and of numerous other workers on the continuity and behavior of the gaseous and liquid states was developed by experimentation on pure substances and mixtures. Texts and summaries covering phase behavior appeared in the period from 1900 to 1910 (8, 12, 34, 41, 52, 53) and apparently ended the active theoretical investigations on this subject. Most texts in physics or physical chemistry since 1910 have completely eliminated discussions or references to the behavior of binary fluid mixtures under pressures and temperatures approaching the critical conditions, and have limited phase discussions to pure substances or to mixtures at atmospheric pressure. Thus the information concerning phase behavior accumulated in large quantities did not become a background for the average scientifically trained person entering industry during the third and fourth decades of the twentieth century.

The petroleum industry recognized that pressure was a significant variable in phase behavior of their products, probably during the period 1920 to 1930; within a few years several papers (4, 10, 42) gave experimental data on the phase behavior of hydrocarbon mixtures under pressure. In 1932 (36) one explanation for the condensation of a water-white hydrocarbon oil accompanying production of gas from the Big Lake Field, Texas, took the form of a suggestion that the increase of the vapor pressure of a liquid due to gas pressure would increase the concentration of normally liquid constituents in the gas phase. At about this time the early literature received some attention (4, 9), and Kuenen's term "retrograde condensation" was loosely and variedly applied to phase changes occurring at temperatures above the critical temperature or at pressures above the critical pressure of the mixture.

The lack of a common understanding of the exact phenomena to which retrograde condensation applied became apparent during attempts to develop a specific and inclusive nomenclature for the behavior of oil and gas mixtures under high pressure (20). Different interpretations of the meaning of retrograde condensation were made, although there was usually a common agreement as to the expected phase behavior of mixtures. Accordingly, it seemed unfortunate that the term had ever been used if its use resulted in confusion.

The purpose of this paper is to describe the phase behavior of simple and complex fluids, including any condensation phenomena which may be considered retrograde. The development will include pure substances, binary mixtures, concepts of vapor-liquid equilibria, and new data on a complex hydrocarbon system. Following this description of phase behavior, the terminology and usage of retrograde condensation will be discussed. The term "double retrograde condensation" will be taken from the past and introduced into the new order of phase behavior. The significance to the petroleum industry of phase behavior which might be termed "retrograde" is discussed.

Phase Behavior of Pure Substances

The phase behavior of pure substances in the fluid state was the basis for the studies of binary or complex mixtures. The nomenclature of pure substances was the basis for descriptions of the behavior of mixtures.

Cagniard de la Tour in 1822 first described the sudden disappearance of the liquid-vapor meniscus, when ether is heated in a glass tube, as the sudden reduction of the liquid to vapor (6). As a result of liquefaction and density experiments under pressure, Faraday (13) in 1845 predicted "Cagniard de la Tour's state" for carbon dioxide to be 90° F. (87.8° F. critical temperature). In 1869 Andrews (2) reported for carbon dioxide the pressure-volume data and temperature above which two phases could not be visibly observed. He refers to this temperature as the critical temperature.

Up to this time the term "gas" was used to designate a substance occurring close to atmospheric conditions which expanded indefinitely to fill the container, and "liquid", a substance adapting itself to the shape of the container but not capable of indefinite expansion. Thus, when normally gaseous substances were compressed isothermally at temperatures above the critical temperature and no dense phase appeared, the gas was held to be incapable of liquefaction and the sub-
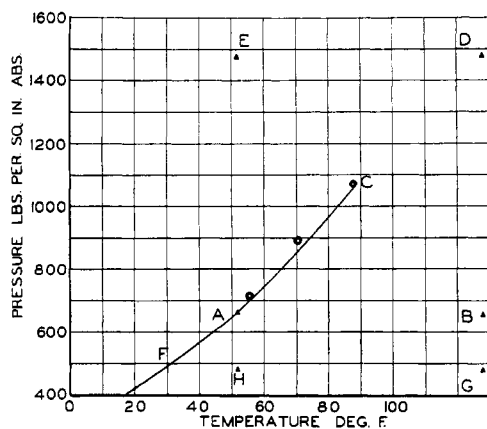

FIGURE 1. VAPOR PRESSURE OF CARBON DIOXIDE

——— Amagat (1)   O Andrews (2)

stance may have been referred to as a gas in this compressed condition. Andrews realized the confusion which would arise if the terms "liquid" and "gas" or "vapor" were used to represent a substance in the fluid state at high pressures, especially in the neighborhood of the critical point; and so he pointed the way to a clear understanding of the fluid state of pure substances.

Figure 1 gives the vapor pressure curve or phases of carbon dioxide in the fluid region. On curve FAC vapor and liquid are in equilibrium. Carbon dioxide at H will undergo no phase changes as it is being compressed until point A is reached. At conditions A a more dense phase called "liquid" will form, and upon compression the entire amount of carbon dioxide will be changed to liquid. Further compression will compress the fluid to conditions E with no abrupt changes. At A the phase change is accompanied by the removal of heat, and such properties as density and viscosity are abruptly changed. As the temperature at which a similar phase change occurs by compression is raised toward C, the abruptness decreases until at C, continuous changes accompany the compression. Figure 2 shows the densities of the vapor and of the liquid on line FAC, and at C the densities of the two phases become indistinguishable.

In a discussion of the terms "liquid" and "gas" or "vapor" in the continuous fluid region away from curve FAC, Andrews (2) points out that the compression of a normal gaseous substance from atmospheric pressure, such as below G, to some high pressure, such as D, does not cause any visible phase change. Likewise cooling from D to E and subsequent expansion to A do not cause visible phase changes or abrupt change in properties, yet at A the substance will begin to form a less dense phase or vapor. Hence normal gaseous carbon dioxide (at atmospheric pressure and 100° F.) after compression, cooling, and expansion without any phase change begins to vaporize, and is shown to be in the liquid state. Such gradual changes can convert a vapor on line FAC to a liquid on FAC by passing around point C. An attempt to use the phase name at the beginning of the path to designate the phase while passing from A-B-D-E-A results in applying the term "vapor" to the substance at the end of the path when it

is a liquid, or of arbitrarily stating that a continuous change such as B to D or D to E constituted a change from vapor to liquid, both of which are inconsistent. The terms "vapor" or "gas" and "liquid" have significance only when on the vapor pressure curve or in the presence of each other, and all stages between these two states are continuous.

Figure 3 was prepared from data on propane in an effort to portray Andrews' concept of "the continuity of the gaseous and liquid states of matter". The pressure-temperature diagram is shaded according to the density of the substance. It shows that only paths which cross $0C$ have abrupt changes in density, and that these changes become less sudden and disappear at C, the critical point. If atmospheric conditions are in the light area for a substance, it is called a normal gaseous substance, and if in the dark area, it is classified as a liquid under ordinary conditions. If an investigator started with a substance in one of these areas on a series of experiments in which pressure and temperature were varied but no signs of a phase change occurred, he would usually refer to the substance throughout the experiment by the name of the phase with which he started. This practice caused little difficulty until the time of Andrews when pressure and temperature changes became large and transcended from a light shading to a dark shading. The practice of labeling a fluid as either liquid or gas and the incompatibility of this custom with the behavior of a substance at pressures and temperatures above the critical point was the occasion for the warning on nomenclature by Andrews (2).

Phase Behavior of Binary Mixtures

Closely following the work on pure substances were the experiments on gaseous or fluid mixtures. Hundreds of articles have appeared on the phase behavior of mixtures, beginning with Cailletet (7), van der Waals (51), Andrews (3), Kuenen (29), and culminating in general review articles and books by Kuenen (34), Duhem (12), Caubet (8), and Rooze-
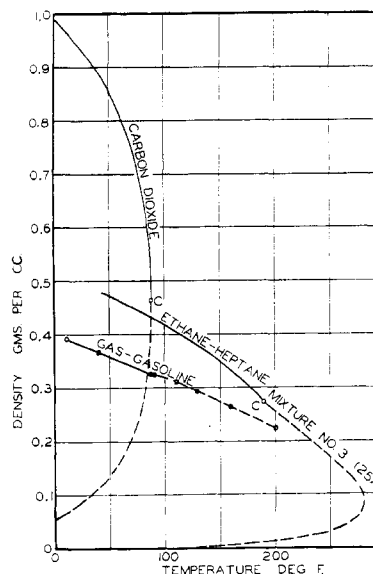

FIGURE 2. DENSITY OF SATURATED LIQUIDS AND VAPORS

boom (41). Table I lists mixtures upon which phase data have been reported. This table is not complete but shows clearly the two periods of study, 1880 to 1902 for data to substantiate or devise theories on the behavior of mixtures, and 1932 to date on the behavior of the petroleum hydrocarbons.

The early work was practically always associated with the theoretical behavior of mixtures, usually with the behavior of pure substances as a standard. One component may have been looked upon as an impurity or the work may have the title used by Villard, "The Solution of Liquids and Solids in Gases" (*49*). He gave qualitative data on the vaporization or sublimation of bromine, iodine, camphor, and paraffin by increase of gaseous pressure of oxygen, air, hydrogen, methane, or ethylene gases over these substances. This and many other papers did not view their data as applying to a two-component system, but as the deviation of one of the constituents from its behavior as a pure substance.

Kuenen, as a student of van der Waal's theories, appears to have had the clearest conception of phase behavior because he predicted qualitatively the phase behavior of binary mixtures. His concepts were nearly always discussed in terms of three dimensions. Kuenen (*29*) introduced the term "retrograde condensation" in describing the phase behavior of carbon dioxide and methyl chloride mixtures. Because the use of this term is not fundamental to an understanding of phase behavior and because views on its exact meaning are conflicting, it will not be used prior to the discussion on nomenclature.
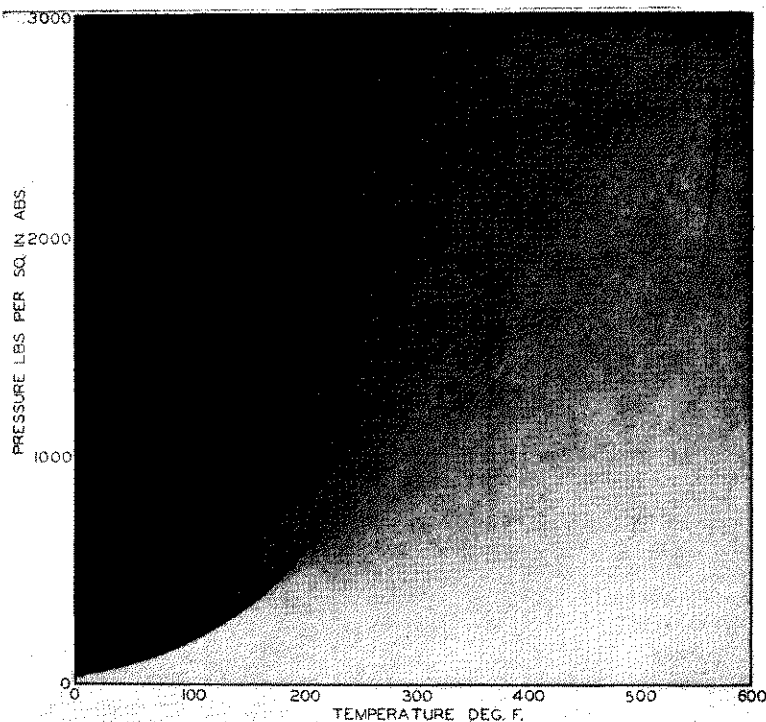
FIGURE 3. CONTINUITY OF GASEOUS AND LIQUID PHASES

TABLE I. MIXTURES UPON WHICH PHASE DATA HAVE BEEN REPORTED

Constituents in Mixture	No. Mixtures Studied	Investigator	Year Reptd.	Citation
CO₂, N₂	3	Andrews	1887	(*3*)
CO₂, air	1	Cailletet	1880	(*7*)
CO₂, air	1	Van der Waals	1881	(*51*)
CO₂, methyl chloride	4	Kuenen	1892	(*29*)
Ethane, N₂O	5	Kuenen	1895	(*31*)
CO₂, ethylene	1	Kuenen	1897	(*32*)
Ethylene, ethane	5	Kuenen	1897	(*32*)
Ethane, CO₂	4	Kuenen	1897	(*32*)
Ethane, butane	2	Kuenen	1899	(*33*)
Methyl ether, HCl	1	Kuenen	1901	(*23*)
CO₂, H₂	3	Vershaffelt	1899	(*48*)
CO₂, SO₂	8	Caubet	1902	(*8*)
CO₂, methyl chloride	10	Caubet (Hartman)	1902	(*8*)
CO₂, nitrobenzene	8	Kohnstamm and Reeders	1912	(*27*)
O₂, N₂ (air)	1	Kuenen and Clark	1917	(*35*)
Soln. of benzene, triphenylmethane, phenanthrene, and resorcinol in ethanol	..	Schroer	1929	(*44*)
Gasoline, naphtha	2	Bahlke and Kay	1932	(*4*)
Pentane, heptane	3	Cummings, Stones, Volante	1933	(*10*)
Methane, propane	6	Sage, Schaafsma, Lacey	1933	(*42*)
Ethane, heptane	8	Kay	1938	(*25*)
Ethane, butane	5	Kay	1939	(*26*)
Methane, N₂, pentane, etc.	..	Boomer, Johnson, Piercey	1937	(*5*)
Natural gas, gasoline	1	Katz, Vink, David	1939	(*24*)
Propane, isobutylene	..	Scheeline and Gilliland	1939	(*43*)
Propylene, isobutane	..	Gilliland and Scheeline	1939	(*18*)
Propane, H₂S	..	Gilliland and Scheeline	1939	(*18*)
Propane, n-butane	6	Nysewander, Sage, Lacey	1940	(*38*)
Methane, pentane	..	Taylor, Wald, Sage, Lacey	1939	(*46*)

Figure 4 is a reproduction of Kuenen's figure (*30*) showing the phase relations of mixtures of carbon dioxide and methyl chloride. AC_2 and BC_1 are the vapor pressure curves of pure carbon dioxide and pure methyl chloride, respectively. DP-RE is the border curve between the single phase and two phases for a mixture of 40 volume (gas) per cent carbon dioxide and 60 volume per cent methyl chloride. Entrance to the two-phase region through curve DP causes a less dense (vapor) phase to appear, and the single phase on the curve is a bubble-point (saturated) liquid. Entrance to the two-phase region through ERP causes a more dense phase (liquid) to

appear, and the single phase is a dew-point (saturated) vapor phase. P is the critical point (called "plaitpoint" by Kuenen), and R is the maximum temperature for the existence of two phases (called the "critical point of contact" by Kuenen). Curve C_2 $P''PP'C_1$ is the locus of the critical points for all possible mixtures of carbon dioxide and methyl chloride. $P''R''$ and $P'R'$ represent possible border curves for mixtures having high and low percentages of carbon dioxide, respectively.

Within the border curve the system divides into two phases. Lines of constant percentage vapor or liquid follow parallel to the border curves and intersect at P, the critical point. The shape of the curves indicates at temperatures between P and R that a dew-point vapor on ER may be compressed to change the equilibrium phases into part liquid and part vapor, but that upon further compression to curve PR, the system would again be all vapor. Kuenen's data (Table II) show quantitatively the results of a compression for the system indicated. This type of behavior does not occur for pure substances or for mixtures below the critical temperature of the mixture.

TABLE II. KUENEN'S PHASE DATA (*29*) ON 59 PER CENT METHYL CHLORIDE–41 PER CENT CARBON DIOXIDE AT 105° C.

Total Vol.	Vol. of Liquid	Pressure, Atm.	Total Vol.	Vol. of Liquid	Pressure, Atm.
117.9	0	73.3	77.3	4.3	83.1
99.6	3.9	77.2	75.3	4.7	83.3
81.2	8.2	81.8	75.4	2.8	83.5
81.0	8.6	81.8	74.3	2.5	83.8
78.6	7.6	82.4	74.0	0	83.8

The more recent measurements on binary hydrocarbons systems are more quantitative than the earlier work, since the object of obtaining the data was to permit quantitative computations rather than to test some theory. Table I includes some mixtures having critical pressures considerably in excess of those for the pure constituents with the corresponding changes in the border curves of the mixtures. This
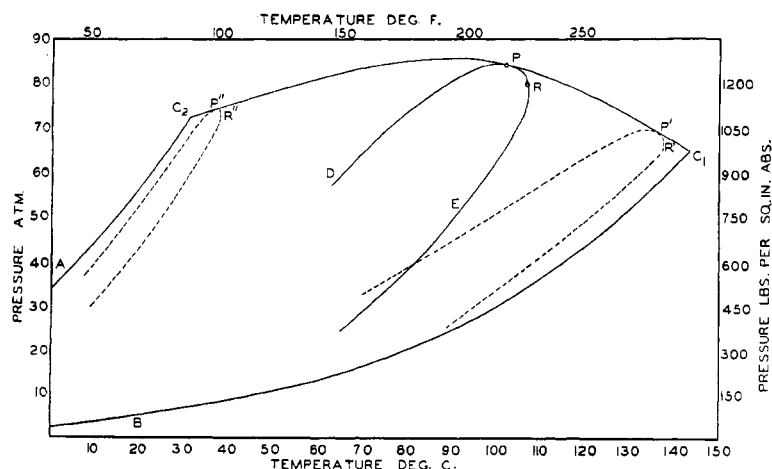
FIGURE 4. KUENEN'S DIAGRAM FOR CARBON DIOXIDE–METHYL CHLORIDE SYSTEM

FIGURE 5. PRESSURE-TEMPERATURE DIAGRAM FOR KAY'S ETHANE-HEPTANE SYSTEM

is true for the border curves of the ethane-heptane system by Kay (25) shown in Figure 5. In addition to border curves, the densities in the single phase at the border conditions or throughout the single-phase area are often obtained. This complete data on a system gives a basis for predicting vapor-liquid equilibria, critical conditions, densities of phases, as well as general thermodynamic properties of mixtures. The behavior of the binary mixtures reported recently is in general accord with the theory and data gathered prior to 1900. One point of interest reported by Schroer (44) and later by Kay (25) is the double inflection in the density curves of the saturated vapor and liquid as plotted on Figure 2 for one of the ethane-heptane mixtures.

Concepts of Vapor-Liquid Equilibria

The early work on phase diagrams did not give data on the quantities of vapor and liquid present in the two-phase region,
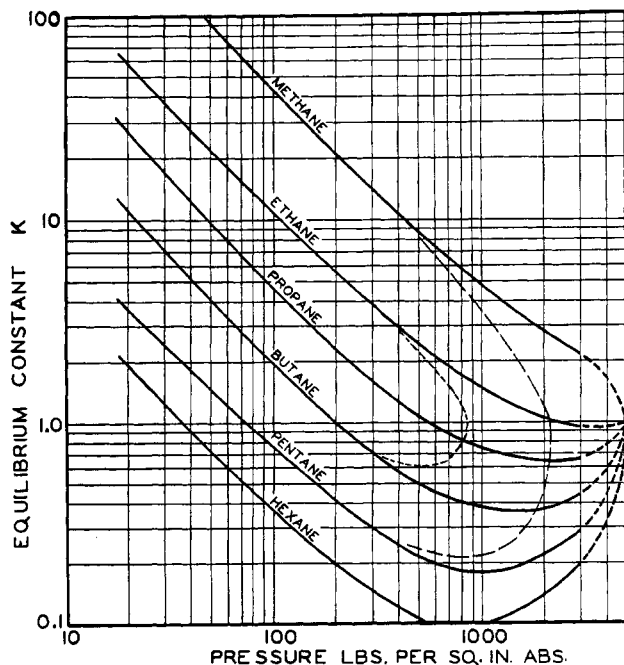

FIGURE 6. CHANGES OF EQUILIBRIUM CONSTANTS WITH PRESSURE AT 200° F.
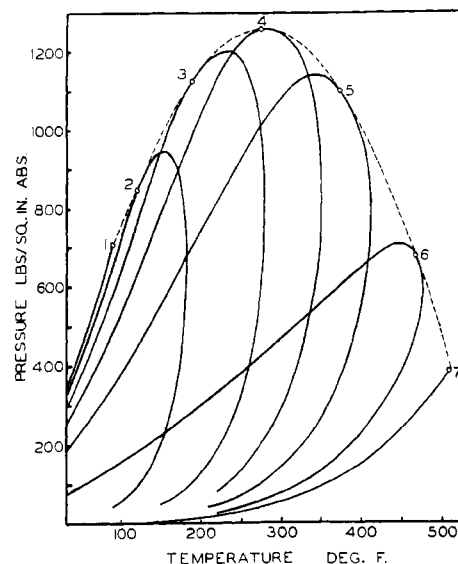
——— (23)   – – – – (26)   — — — (46)

nor did it develop a method of predicting the border curves for mixtures of two or more substances. This lack of quantitative treatment may have caused the workers who were predicting the properties of fluid substances to develop concepts independent of the early work on phase behavior. Raoult's and Dalton's laws were utilized to predict bubble points, dew points, and the percentage and composition of vapor and liquid coexisting in the two-phase region. The vapor pressure data of pure substances were utilized to predict the properties of mixtures. Solubility investigations (17, 37) spoke of the solubility of gases in liquids without considering the mixtures from the standpoint of the phase behavior of binary systems obtained in earlier days.

In 1932 Raoult's and Dalton's laws were superseded by equilibrium constants (45) as obtained from fugacities. The equilibrium constants permitted vaporization computations for constituents above the critical pressure and at conditions where deviation from ideal gas laws could not be neglected (22). The effect of gas pressure upon the vapor pressure of a substance, the Poynting effect, was used to give the behavior of substances. These concepts were uppermost in the minds of the investigators who were active during the early discussions of the phenomena which has caused the term "retrograde condensation" to be commonplace.

Lacey (36) in 1932, discussing the possible causes of production of water-white liquid hydrocarbons from a well said: "My picture would be based upon two things; first the well known fact that, at high pressures, liquids have higher vapor pressures than is ordinarily the case. At considerably higher pressures such as 3000 or 4000 pounds, which Mr. Foran (14) speaks of, that effect is quite marked. . . . . Also, the fact as brought out in preliminary work by the Institute on Project 37 . . . . . indicates very definitely that when natural gas is brought into contact with crude oil at high pressures and at relatively high temperatures, such as 170° to 200° F., not only does gas dissolve in the oil, but constituents of the oil as originally put in the container travel over into the gas."

The reports of the phase data on the methane-propane system, the pentane-heptane systems, and the gasoline and naphtha gave the phase behavior both from the standpoint of the phase diagram and from the concept of vapor-liquid equilibria. The division of a mixture into vapor and liquid

could be predicted for the binary systems from the equilibrium constants derived from the phase data.

The equilibrium constants for the volatile constituents of the natural gas–crude oil system (23) showed the rise of the values of the equilibrium constants back towards unity as shown in Figure 6. These data showed that natural gases in equilibrium with crude oil at pressures above 600 to 1000 pounds would contain a higher percentage of the less volatile constituents than at a lower pressure. The removal of a saturated gas from a crude oil at 2000 pounds and isothermal expansion to 1000 would be expected to cause condensation.

The approach of the values of the equilibrium constants to unity at the critical pressure of a mixture was known in 1933 (10, 22). A comparison of the methane-propane, ethane-heptane, and natural gas–crude oil systems (21) indicated that equilibrium constants have a regular pattern of convergence to unity, and that the constants for a constituent were not behaving abnormally because the equilibrium constant for this constituent varied with the mixture at pressures approaching critical pressures for the mixtures in which the constituent was present. An isothermal plot (Figure 6) will clarify this convergence of the equilibrium constants to unity. It is now known that in binary mixtures the convergence pressure is the critical pressure of the particular binary mixture which has for its critical temperature the temperature at which the constants are desired. This convergence pressure is not directly dependent upon the over-all composition of the mixture for which the constants are desired. The locus of the critical pressures for the ethane-heptane system (Figure 5) shows that the pressure for convergence to unity would vary from 850 pounds at 120° F. to 1263 at 277° to 682 at 468°.

Complex mixtures which may be assumed to be composed of two components, each of which is a multicomponent mixture, may correspond to the same general behavior as binary mixtures. A clearer concept of equilibrium-constant behavior is obtained by following the concept that the convergence pressure is a function of the critical pressure corresponding to the mixture of the two components, which has for its critical temperature the temperature of the equilibrium than is obtained by focusing attention on the over-all composition of the system for which the constants are to be used. Clarification of this idea for mixtures and methods of predicting critical pressures will give reliable equilibrium constants in the range of the critical conditions or for that portion of the phase diagram for a given mixture which is above the critical temperature.

This concept of the influence of the critical point upon vapor-liquid equilibria was slow to be accepted by present-day investigators. However, Caubet's paper on liquefaction of gaseous mixtures, including a plot of vapor and liquid compositions as a function of pressure for a carbon dioxide–sulfur dioxide mixture (8) is suggestive of this fundamental relation. Vapor-liquid equilibria computations using the equilibrium constants have developed the general shape of the phase diagram for complex mixtures. The experimental phase diagram which is to be presented now does not deviate materially from previous concepts.

Experimental Data on Phase Diagram of a Complex Mixture

New data on the behavior of a mixture of natural gas and natural gasoline are presented to show the phase behavior of complex mixtures in the critical region. Bahlke and Kay's report (4) on gasoline and naphtha included the border curves as well as the percentage liquid within the two-phase region. These data and others giving portions of the border curves for complex mixtures (37) do not show a clear picture of the phase behavior in the vicinity of the critical point. Experi-

mental data similar to those recently reported (24) giving the quality lines near the critical point for a mixture of natural gas and natural gasoline will be presented. The phase behavior of a natural gas–natural gasoline mixture (Table III) was observed visually through glass over a temperature range of 11° to 200° F. and a pressure range of 600 to 2900 pounds per square inch.

The apparatus used (Figure 7) consisted primarily of a Jerguson gage, A, with glass windows, B. Pressure was supplied by mercury pump C and measured by a calibrated Bourdon gage, D. Agitation to ensure equilibrium was obtained by rocking

TABLE III. LIQUID AND VAPOR VOLUMES FOR MIXTURE OF NATURAL GAS AND NATURAL GASOLINE

Abs. Pressure Lb./sq. in.	Vol. of System Cc.	Vol. of Liquid Cc.	Abs. Pressure Lb./sq. in.	Vol. of System Cc.	Vol. of Liquid Cc.
Temperature 11° F.			Temperature 110° F.		
2320	24.0	Single phase	3075	29.1	Single phase
2278	24.2	Single phase	2807	29.9	Single phase
2272	24.2	23.5	2783	30.2	Single phase
2262	24.2	21.1	2777	30.6	2.3
2247	24.2	19.7	2775	30.6	6.0
2213	24.7	17.5	2758	30.6	8.8
2200	24.8	17.0	2740	31.0	9.6
2137	25.2	15.3	2701	31.4	10.4
2028	26.4	13.8	2662	31.8	10.4
1927	27.7	12.6	2685	32.1	10.3
1820	29.6	12.2	2548	33.6	10.4
1651	33.2	11.0	2355	36.1	10.1
1440	39.2	10.1	1968	44.0	9.1
1262	47.1	9.5	1795	49.0	9.2
1062	59.3	9.0	1298	70.8	8.0
915	71.9	8.9	1010	94.1	7.7
730	95.1	8.4	827	117.8	7.4
605	117.8	7.3			
Temperature 40° F.			Temperature 130.0° F.		
2890	25.2	Single phase	2838	32.2	Single phase
2558	25.5	Single phase	2800	32.5	2.5
2524	25.9	Single phase	2795	32.5	3.7
2515	25.9	24.1	2785	32.5	5.2
2502	25.9	20.1	2777	32.5	5.5
2452	26.2	15.9	2763	32.7	6.5
2437	26.4	15.3	2727	33.0	7.8
2395	27.0	14.8	2712	33.5	8.3
2312	27.9	13.5	2665	34.0	8.6
2187	29.6	12.8	2575	35.2	9.0
2048	31.8	12.0	2522	36.3	9.2
1893	34.6	11.2	2410	37.8	9.0
1662	40.6	10.5	2264	40.5	9.0
1495	46.4	9.6	2020	45.5	8.3
1073	68.6	8.5	1775	52.8	8.2
838	91.8	7.8	1338	73.1	7.8
687	115.5	7.6	1065	94.4	7.4
			882	116.8	6.4
Temperature 87.5° F.			Temperature 160.0° F.		
2901	28.4	Single phase	2798	36.1	Single phase
2738	29.0	Single phase	2785	36.1	0.9
2720	29.1	Single phase	2775	36.1	1.4
2715	29.1	14.7	2767	36.3	2.0
2713	29.1	14.3	2757	36.5	2.5
2700	29.3	13.7	2738	36.7	3.7
2685	29.4	13.4	2665	37.6	5.5
2662	29.7	13.1	2612	38.5	6.2
2649	29.9	12.8	2560	39.4	6.7
2623	30.2	12.6	2525	39.8	6.9
2585	31.0	12.5	2426	41.5	7.3
2524	31.6	12.1	2300	43.8	7.3
2400	33.2	11.4	2165	47.2	7.8
2245	35.8	11.0	1923	53.8	7.6
2098	38.5	10.8	1482	72.0	7.1
1412	60.5	9.2	1175	93.2	6.7
1250	69.8	9.0	962	115.7	5.9
980	92.3	8.2			
805	114.8	7.6			
Temperature 92° F.			Temperature 200.0° F.		
3050	27.9	Single phase	2955	39.0	Single phase
2763	29.1	Single phase	2688	41.9	Single phase
2738	29.2	Single phase	2674	42.1	Single phase
2737	29.2	10.3	2662	42.3	Single phase
2736	29.5	12.1	2658	42.3	Single phase
2732	29.5	12.1	2640	42.5	0.1
2726	29.5	12.3	2628	42.8	0.6
2715	29.5	12.3	2590	43.1	1.3
2700	29.5	12.1	2550	44.0	2.0
2655	30.0	11.9	2488	45.1	2.9
2618	30.6	11.7	2401	46.9	3.8
2532	31.6	11.3	2320	49.0	4.4
2367	34.0	11.2	2245	50.8	4.8
2170	37.1	10.3	2114	54.2	5.2
1750	46.9	9.1	1937	59.6	5.2
1260	69.6	8.7	1740	67.5	5.6
977	92.7	7.9	1624	72.7	5.4
810	114.2	7.4	1305	92.9	5.5
			1070	115.8	5.4

the entire gage assembly around axis *E-F*. A constant-temperature air bath, *G*, controlled the temperature of the Jerguson gage. Temperature measurements were made by thermocouples embedded in gage walls and by a mercury-in-glass thermometer in the air bath. The scale beside the glass window was used to calibrate the volume of the gage by mercury displacement. This scale measured the position of the gas-liquid meniscus, if present, and the location of the hydrocarbon-mercury meniscus.

decrements from the single-phase region to within the two-phase area. After each volume change of the system, the Jerguson gage was agitated by rocking before any readings were taken.
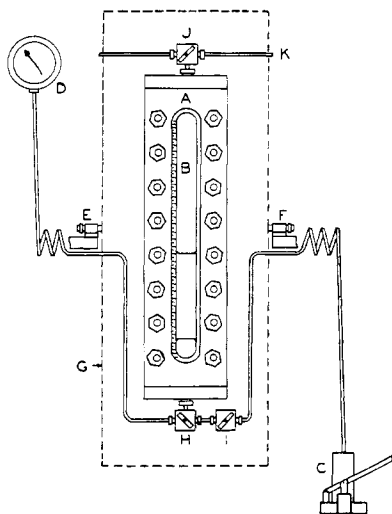
FIGURE 7. APPARATUS FOR MEASURING PHASE VOLUMES

Volume measurements were made on a mixture of 83.5 cc. of gas at 1100 pounds per square inch/gage and 87° F. and of 6.70 cc. of natural gasoline at 60° F. (Table IV). Valve *J* was closed and all volume changes on the system were made by changing the mercury level in the gage. The procedure for obtaining the phase behavior was to drop the pressure isothermally in small

TABLE IV. COMPOSITION OF NATURAL GAS-NATURAL GASOLINE MIXTURE

	Mole Fractions		
Constituent	Natural gas	Natural gasoline	Mixture
N_2	0.0043	....	0.0036
CO_2	0.0051	....	0.0043
Methane	0.9320	....	0.7841
Ethane	0.0425	....	0.0357
Propane	0.0161	....	0.0135
Butanes	.....	0.081	0.0129
Pentanes	.....	0.398	0.0632
Hexanes	.....	0.281	0.0446
Heptanes and heavier	.....	0.240[a]	0.0381
Mol. weight	17.2	83.1	27.6
Gr., ° A. P. I.	.....	78.3	273[b]

[a] Density 0.733 grams per cc., mol. weight 107.
[b] At 60° F. and 2620 pounds per square inch.

At 40° F. the pressure drop to 2515 pounds showed a small portion of gas phase, and hence the entrance to the two-phase system was through the bubble-point curve. The volumes of the system and liquid phases for isotherms are given in Table III. For the 110° F. isotherm, a pressure drop to 2777 pounds showed a small amount of liquid, and hence the entrance to the phase diagram was through the dew-point curve. The effect of small pressure changes upon the relative amounts of vapor and liquid as the two-phase area is entered is pronounced for the isotherms in the neighborhood of 90° F. (Figure 8). At 87.5° F. a pressure drop estimated as 5 pounds changed the single phase into 50.5 per cent liquid and 49.5 per cent vapor.

The phase diagram for the system (Figure 9) is a plot of the pressures for even values of volume per cent liquid taken from the isotherms of Figure 8. The per cent liquid lines converge
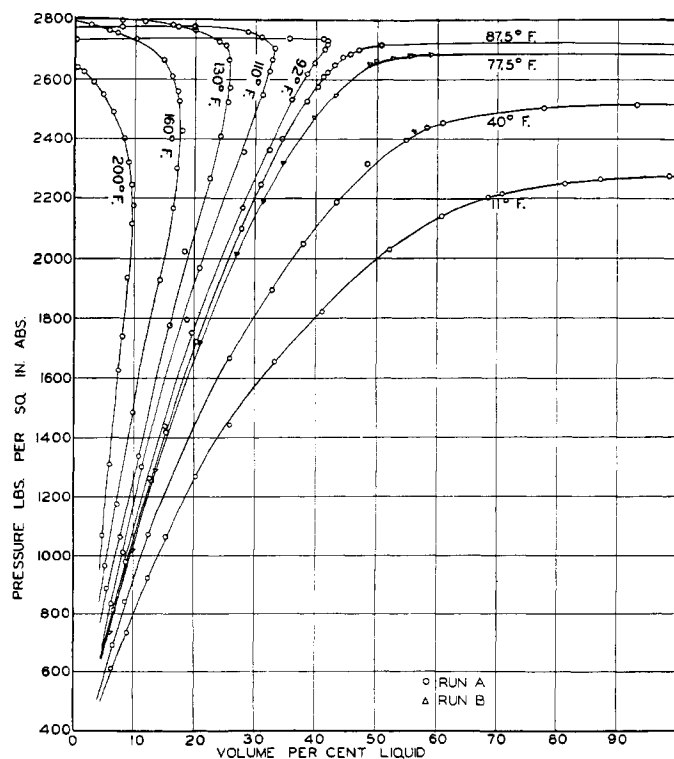
FIGURE 8. PERCENTAGE LIQUID ISOTHERMS FOR NATURAL GAS-NATURAL GASOLINE MIXTURE
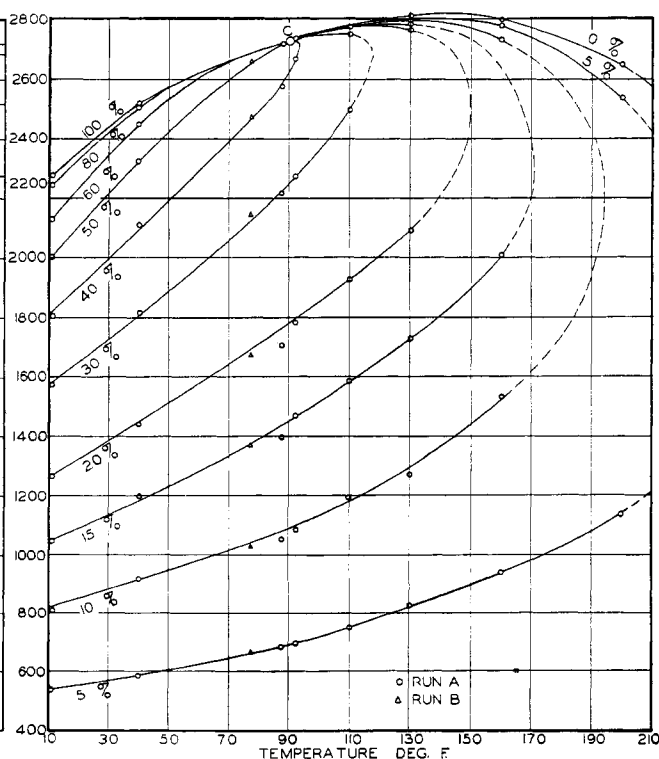
FIGURE 9. PHASE DIAGRAM OF NATURAL GAS-NATURAL GASOLINE MIXTURE

to C (2730 pounds per square inch absolute and 90° F.), the critical point of the mixture. At temperatures above the critical, successive pressure drops show liquid per cent increases followed by decreases. At temperatures below the critical the successive pressure drops show increases in the per cent vapor. The behavior of this system is similar to that of a natural gas–natural gasoline mixture recently reported (24), and the mixture used has a position on the locus of the critical points for all mixtures of the gas and gasoline corresponding approximately to curve 3, Figure 5.
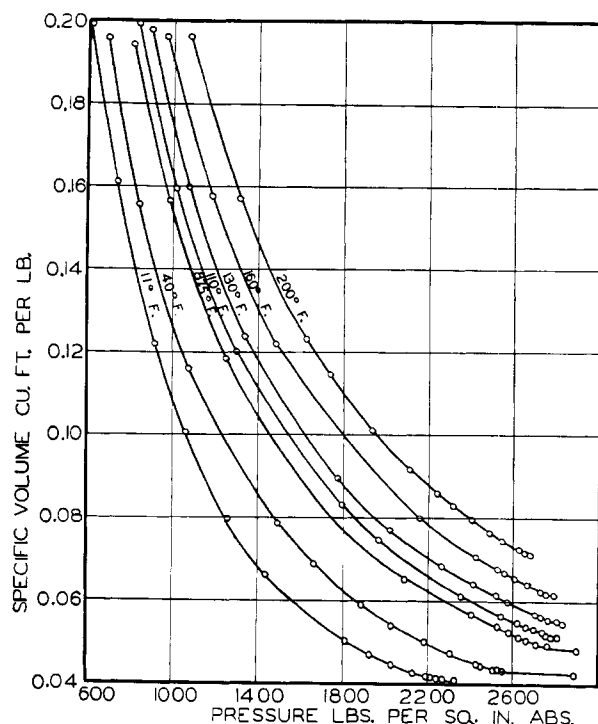
FIGURE 10. SPECIFIC VOLUMES OF TWO-PHASE SYSTEM

A consideration of phase changes accompanying pressure and temperature changes shows that a saturated vapor at 110° F. and 2780 pounds will change to 70 per cent vapor and 30 per cent liquid by volume as the pressure is dropped to 2750 pounds. Further isothermal pressure reduction to 2700 pounds causes the liquid to increase to a maximum of 33 volume per cent liquid, and lower pressures revaporize the liquid. Although the phase diagram indicates no change in the per cent of liquid over a considerable range, visual observations show portions of the vapor to be condensing and portions of the liquid to be vaporizing simultaneously.

Experimental data on three mixtures of another gas and the gasoline indicate that the locus of the criticals and the shape of the phase diagrams are similar to those of binary mixtures.

Readings of the temperature, pressure, and volume were made to ±0.2° F., ±3 pounds, and ±0.2 cc., respectively. The critical conditions should be 90° ± 1.5° F., 2730 ± 10 pounds per square inch, and 20.2 ± 0.6 pounds per cubic foot. A few of the points on the phase diagram indicate greater deviations than those indicated above, possibly due to failure to reach equilibrium.

The points at 77.5° F. for run B were made on a mixture metered to the gage at the same ratio of gas to liquid as was used in run A.

The composition of the mixture was computed from the low-temperature fractional analyses of the gas and gasoline given in Table IV.

The specific volumes of the mixture in two phases as computed from the quantity of gas (4.96 grams), the quantity of gasoline (4.52 grams), and the volume measurements are plotted in Figure 10. The density at the border curve is plotted in Figure 2 and shows that the saturated liquid and saturated vapor densities on the border curve may have an inflection at the critical point. The similarity of the curves of Figure 10 for isotherms above and below the critical temperature indicates the necessity of the close approach of the vapor and liquid densities in the two-phase region near the critical, since large variations in liquid vapor ratios have little effect on the density of the entire system.

Opalescence or color effects were observed along the border curve from the 77.5° F. point to the 130° point. The colorless single phase turned to a reddish brown (transmitted light) at a pressure within 5 to 10 pounds of the border curve during isothermal pressure reduction. The fluid is bluish white to reflected light. As the fluid divides into two phases, a portion of the color is retained in both phases for a pressure drop of 5 to 20 pounds below the border curve. This color phenomenon is less pronounced at temperatures below and above the critical but does not have the abrupt change at the critical point reported by Roess (40) for petroleum fractions. This peculiar appearance is believed to be caused by the scattering of light on tiny surfaces (19, 47, 54). Agitation and time up to 30 minutes appear to have no effect on the color stability.

This description of phase behavior of mixtures and related concepts of vapor-liquid equilibria without using the term "retrograde condensation" demonstrates that the term is not fundamental.

Retrograde Condensation Nomenclature

Kuenen gave the name "retrograde condensation" to an isothermal compression process in which a saturated vapor changed to part liquid and then the liquid decreased until the system was again a saturated vapor (Table II). A review of Kuenen's works indicates to the authors that he referred to the compression process as being a condensation of the entire system and did not intend condensation to mean exclusively the formation of a more dense phase or liquid. The term "retrograde" denotes "contrary to the previous direction", and the authors believe that Kuenen referred to the disappearance of the liquid during compression as retrograde condensation (first kind).

FIGURE 11. SYSTEM FOR RETROGRADE CONDENSATION (SECOND KIND)

Later Kuenen worked on retrograde condensation of the second kind (31) in which the phase diagram had the critical point at a position corresponding to P' on Figure 11. At temperatures between P' and R', compression causes the saturated liquid on $R'R'$ to vaporize, and further compression until the border curve is reached again causes the mixture to return to the liquid state. Because Kuenen referred to compression processes below the critical temperature as normal condensation, the term "retrograde" must have referred to that portion of the process which went opposite to the accustomed direction. In order to have retrograde behavior, there must be a normal behavior for reference, and the reference

was the behavior of pure substances or that of mixtures at temperatures and pressures below the critical.

Kuenen always referred to compression processes although he stated that the opposite phenomena would occur upon expansion. He did not discuss isobaric changes. Duhem (12) and Caubet (8) adopted a nomenclature of retrograde condensation for all isothermal or isobaric processes having a reversal in the formation of liquid or vapor when traveling continuously from dew point to dew point, and used retrograde vaporization for similar phenomena between bubble points. If Kuenen's condensation referred to the condensation of the entire system, then opposite nomenclature to denote all processes for which reversals might occur would be retrograde expansion and the isobaric phenomena of retrograde heating and retrograde cooling. No consistent nomenclature based on simple premises can be found among the early workers.

FIGURE 12. PHASE DIAGRAM TO ILLUSTRATE NOMEN-
CLATURE OF RETROGRADE CONDENSATION

A long period intervened between the writings of early work on retrograde phenomena and the present-day development of the term. Papers (4, 10, 25) mentioning retrograde condensation do not state whether it was condensation of the system, liquid formation, or vapor formation. Sage, Schaafsma, and Lacey in the A. P. I. re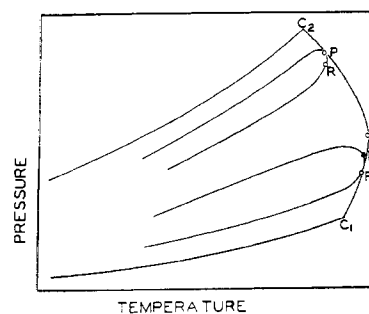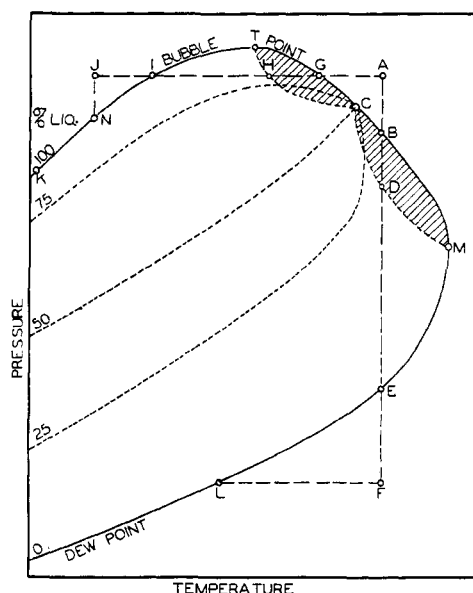ference (42) on the methane-propane system give what is believed to be the general concept. In going over a path similar to AD of Figure 12, they state: "This type of liquid formation upon lowering of pressure is called 'retrograde condensation.'" This definition retains the significance of retrograde as originally used in accord with its meaning of opposite to the accustomed phenomena, if the standard is the condensation or vaporization of pure substances or of mixtures at low pressures. However, the term "condensation" now refers to the formation of a liquid phase and not to the condensation of the entire system. A survey of the literature in the past decade and discussions with scientists familiar with the subject indicate that retrograde condensation interpreted in recent years has been either as a general term applying to all isothermal phase changes above the critical temperature and all isobaric changes above the critical pressure which were opposite to normal behavior, or in accord with the above nomenclature (42) as enlarged to cover all processes (20). This nomenclature is not in accord with Kuenen and Caubet, but it is believed that no simple

rules of nomenclature could be devised which would be in accord with these authors.

The rules which give the recommended nomenclature are as follows: Condensation is interpreted as the formation of a more dense or liquid phase and vaporization is interpreted as the formation of a less dense or vapor phase when the system is on or within the border curve for a two-phase fluid system. The term "retrograde" is used to earmark phase changes in which the direction of the temperature or pressure travel causing the phase change is backward from that which causes the phase change for normal cases, such as pure substances or mixtures at low pressure. At atmospheric pressure, a temperature drop or a pressure rise may cause condensation of a vapor to a liquid. A condition may arise above the critical temperature or pressure of a mixture within the limits of the two-phase region in which a rise in temperature at constant pressure or decrease in pressure at constant temperature causes vapor to change into liquid. This process is condensation, but because the conditions of temperature or pressure are changing in a direction opposite to that normally encountered, the condensation is said to be retrograde.

Figure 12 shows an assumed border curve KNIGCBMEL which might represent a complex mixture. Within the curve both gas and liquid phases are present, and outside of the curve the system is in a single phase. Entrance to within the border curve KNIGC causes a bubble of vapor to appear, and this portion of the border curve is the bubble-point or saturated liquid curve. Likewise entrance to within the border curve through curve LEMBC causes a droplet of liquid to appear, and this portion of the curve is the dew-point or saturated vapor curve.

The mixture in the single phase at A may be expanded to B, at which pressure the first liquid will appear, the upper dew point. Further pressure reduction causes continued condensation until some point, D, is reached, at which pressure the liquid formed begins to vaporize until at pressure E the entire quantity of liquid formed from B to D has been vaporized and the mixture is at its lower dew point. The condensation from B to D is retrograde, and may be further qualified as being isothermal and between dew points. From D to E normal vaporization occurs with expansion.

The fluid at A may be cooled to G, at which temperature a bubble of vapor will appear and grow with further temperature reduction until some point H is reached. From H to I temperature decrease causes normal condensation. The vaporization from G to H is retrograde vaporization, and may be further qualified as being isobaric and between bubble points.

The passing in opposite directions will cause opposite phenomena; for example, from D to B is retrograde vaporization and from H to G is retrograde condensation. Isothermal retrograde phenomenon may occur only above the critical temperature, C, and below the maximum temperature of two phases, M; the isobaric retrograde phenomenon may occur only above critical pressure C but below the maximum pressure of two phases, T. Retrograde phenomena can occur only in the region corresponding to the cross hatching in Figure 12.

Figures 4, 5, and 11 show that the type of the phase diagram may vary. Such diagrams as curve 2 of Figure 5 have their critical point corresponding to I of Figure 12, and the curve of Figure 11 has the critical point corresponding to E of Figure 12. In these cases the same rules of designating the retrograde phenomena will hold—using retrograde as referring to the direction change of pressure or temperature and qualifying the process as isothermal or isobaric and as occurring between bubble or dew points. Kuenen called condensation between dew points "first kind", and between bubble points, "second kind". Only isothermal or isobaric changes are considered retrograde, since a change in phase accompanying a combined variation of pressure and temperature has no standard of comparison. If there is no accustomed direction, there can be no backward motion. For the types of phase diagram where only the bubble point or the dew point line reverses to the critical point, only retrograde phenomena between bubble point or between dew points, respectively, are possible.

Point C (Figure 12) joining the bubble- and dew-point curves is the critical point for the mixture, although point M has been referred to by this name. A plot of the density of the liquid along the bubble-point line and of the vapor along the dew-point line shows the densities become identical at the conditions of C, Figure 2. Likewise a plot of compositions of vapors and liquids shows that they become equal only at C. The behavior at C is truly critical, since a very small change in pressure or temperature will transform a system in the uniform phase to any desired ratio of vapor to liquid. Points M and T are the maximum conditions for the existence of two phases, but at a finite distance below either point only a small quantity of the second phase may exist. No abrupt changes occur at these maximum points. The maximum temperature for the existence of two phases, M, has been called the "cricondentherm" (9, 10, 42).

The continuity of the single-phase fluid region for complex mixtures is similar to that of pure substances. The area of the single-phase region represented by very dark shading of Figure 3 or around J of Figure 12 has been called "liquid" when the entire discussion was limited to that portion of the phase diagram. Likewise the area represented by the light shading of Figure 3 or around F of Figure 12 has been called "vapor" or "gas" when the entire discussion was limited to low pressures. In view of the fact that a discussion of retrograde condensation usually includes reference to the state of a substance near the critical point, it is recommended that the terms "liquid" and "gas" or "vapor" be used only when the system is on or within the border curve. The practices of calling a single phase at J a compressed liquid (meaning a state reached by isothermal compression of a liquid) and the single phase at F a superheated vapor (meaning a state reached by isobaric heating of a vapor) may convey some idea of the properties of the phase, but the extension of this practice to the critical temperature and critical pressure, respectively, may lead to confusion. The identification of a single phase should be made not by terms "liquid" or "vapor", which are reserved for differentiating between two phases, but by the term "fluid" with further qualifications as to temperature, pressure, density, or position on the phase diagram.

The rules of nomenclature applied to the experimental phase diagram (Figure 9) define the formation of 15 per cent by volume of liquid when changing the pressure on the system from 2800 to 2640 pounds at 160° F. isothermal retrograde condensation (between dew points). Likewise the change from a saturated vapor at 2800 pounds and 120° F. to 95 volume per cent vapor and 5 per cent liquid at 2800 pounds and 130° F. is isobaric retrograde condensation (between dew points). The reverse path to those above would cause vaporization which might be called "retrograde" and be qualified in the same manner as the condensation process.

Further consideration of the proposed nomenclature in light of the phase diagram for natural gas–natural gasoline mixture indicates complications if the term is to assume specific scientific meaning. A pressure drop on the system at 170° F. and 2400 pounds would cause the volume percentage of liquid to increase slightly. However, the volume, weight, and number of moles of liquid may not increase for this change in pressure. If the term "retrograde" is to be used for small changes over which the amount of the liquid is changing quantity in the opposite direction for different bases, the basis of measurement must be included with the term. Also, if the term were applied to the components of the mixture, the minima on the equilibrium constant curves show that condensation or change from vapor to liquid state for the different constituents terminates with isothermal pressure reduction at different pressures, neither of which is the same as that corresponding to the maximum quantity of liquid formed on any basis.

The phase behavior of mixtures may be adequately described without use of the term "retrograde condensation", as illustrated by the first portion of the paper. The term is meaningless without qualifications if it is applied to detailed behavior indicated above. The term has less significance as our knowledge of the phase behavior of mixtures at high pressures increases as the standard of comparison becomes mixtures at high pressure rather than the behavior of pure substances, and there are no phenomena opposite to the previous conception. If one considers the term "retrograde" as applying only to the reversal occurring for phase changes during the continuous change of temperature or pressure, then the term is practically removed from usage because most changes in state are from one condition to another with only the initial and final states under consideration.

Double Retrograde Condensation

In experiments on binary mixtures at high pressures it was found that two liquid layers would form, especially when one component was polar. Van der Waals discusses the data on ethane-alcohol and carbon dioxide–nitrobenzene mixtures which formed two liquid layers (50). A saturated vapor of systems of this type might give two liquids instead of the usual single liquid formation by retrograde condensation upon reducing the pressure isothermally at temperatures above the critical. To distinguish the phenomena in which two liquids are condensed or vaporized in a retrograde manner, they were called "double retrograde" condensation or vaporization by van der Waals. The same rules of nomenclature that have been used when one liquid phase is condensed or vaporized will be used when two liquid phases are condensed or vaporized except that the word "double" will prefix the name.

Double retrograde condensation probably would occur for high-pressure natural gases saturated with both heavy hydrocarbons and water vapor. High pressure is known to increase the vapor pressure of water in the water–natural gas mixtures as the critical pressure for these mixtures is being approached. Thus it may be expected that water will condense along with the hydrocarbons if the pressure is decreased isothermally.

The separation of petroleum hydrocarbons into two liquid phases occurs in propane deasphaltizing of oils. Recent experiments (24) show that a mixture of natural gas, propane, and crude oil will form two liquid phases, and that a phenomenon similar to a critical point may be observed between the gas and the lighter liquid phase. Such results indicate that double retrograde condensation producing two hydrocarbon liquids from a gas phase would occur at high pressures for mixtures containing high concentrations of an intermediate constituent between methane and the high-boiling constituent.

The case of isothermal pressure reduction when a gas and liquid phase forms a second liquid phase with increase in total quantity of liquid has not been discussed but it is likely to be a step in the above process. This complication in nomenclature prompts the suggestion that "double retrograde condensation" be reserved for cases where a uniform phase is changed to three phases by isothermal pressure reduction (or isobaric temperature rise), and that all other related phenomena or portions thereof be described in full.

Significance of Retrograde Condensation in the Petroleum Industry

The behavior of petroleum hydrocarbons in the retrograde regions has become of prime interest in the withdrawing of petroleum from the earth and does have an influence on several processing operations.

COMP	MOL. FR.
C₁	0.843
C₂	0.067
C₃	0.042
C₄	0.024
C₅	0.012
C₆	0.007
C₇₊	0.005

983 CU. FT.

1000 LBS.
200° F.

C U. FT.
1000   1000

COMP	MOL. FR.
C₁	0.173
C₂	0.043
C₃	0.054
C₄	0.058
C₅	0.063
C₆	0.078
C₇₊	0.531

0.62 GAL.

COMP	MOL. FR.
C₁	0.862
C₂	0.066
C₃	0.039
C₄	0.020
C₅	0.008
C₆	0.004
C₇₊	0.001

955 CU. FT.

1000 LBS.
100° F.

COMP	MOL. FR.
C₁	0.195
C₂	0.068
C₃	0.101
C₄	0.119
C₅	0.114
C₆	0.120
C₇₊	0.284

1.49 GAL.

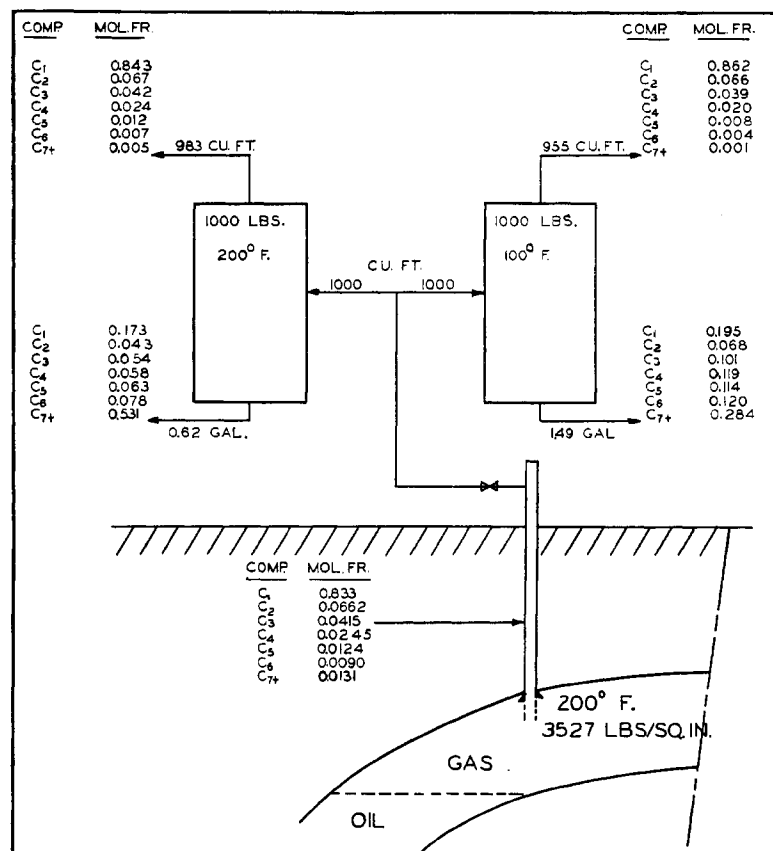| COMP	MOL. FR.
C₁	0.833
C₂	0.0662
C₃	0.0415
C₄	0.0245
C₅	0.0124
C₆	0.0090
C₇₊	0.0131

200° F.
3527 LBS/SQ. IN.

GAS

OIL

FIGURE 13. CONDENSATE FORMATION

In the early days of oil and gas production when the well depths were relatively shallow and pressures were low, an observer could stand at a well head and identify the products as crude oil or natural gas, inferring that they were in the liquid and gaseous state within the earth. The works of Lindsly (37) and others established the solubility of natural gas in crude oil; thus petroleum engineers realize that a well producing 300 to 800 standard cubic feet of natural gas per barrel of crude oil might be producing a saturated liquid phase from the earthen reservoir. This solubility phenomenon was an enlargement of the customary solubility effect known at atmospheric conditions.

The statement that the material from a well producing natural gas and liquid hydrocarbons having normal boiling points as high as 400° or 500° F. could be a saturated gas phase in the reservoir (36) was not an enlargement of the atmospheric pressure vaporization law but a complete contradiction. That increased pressure would vaporize and decreased pressure condense did not appear logical until the behavior of mixtures in the region of the critical point was appreciated.

An example of the effect that pressure changes play in the phase behavior of the effluent from a condensate well is known in Figure 13. The information presented is calculated from the experimental data of equilibrium between natural gas and crude oil (23). A reservoir containing a natural gas which is saturated or in equilibrium with crude oil at 200° F. and 3527 pounds pressure is producing only from the gas phase. Normal production processes create a combination of temperature and pressure drop, such as to 100° F. and 1000 pounds, which causes condensation to the extent of 1.49 gallons of liquid per 955 standard cubic feet of natural gas. The behavior of the well effluent was computed for conditions

of 200° F. and 1000 pounds to show the effect of pressure decrease alone, giving 0.62 gallon of liquid from the same amount of gas as was used at the other conditions. Thus pressure decrease might be credited with 42 per cent of the liquid production at the 1000 pounds and 100° F. The analyses of the liquids condensed indicate the characteristic of condensation by pressure decrease since it has more effect on the high-boiling constituents than on the more volatile compounds. This process at 200° F. may be retrograde condensation (isothermal, between dew points), or it may be a combination of retrograde condensation based on volumetric yield of liquid down to some pressure such as 1100 pounds and normal vaporization from 1100 pounds to 1000 pounds. The isothermal condensation is representative of the behavior which occurs in the reservoir.

The effect of pressure on the condensation of heavy constituents has an important bearing on the production methods suitable for removing high-pressure gases from reservoirs. The usual method of production had been to withdraw the contents of a reservoir and allow the reservoir pressure to drop (39). However, this method would cause high-boiling constituents, if present in the gas phase, to condense along with equilibrium portions of more volatile constituents. It is reported (39) that the liquid yield from the gas from the LaBlanca field has decreased from 9 barrels per million cubic feet of gas at 3800 pounds reservoir pressure to 2.6 barrels per million at 2180 pounds reservoir pressure. Since the condensate in the reservoir only wets the sand and is not expelled from the reservoir as liquid, the condensate is lost except through partial vaporization processes which might occur at low pressures.

The realization that this condensation would occur in the reservoir and the statutes forbidding waste of gas have caused production methods to take the form of recycling operations (11, 15, 16). Recycling consists of production of a gas phase containing high-boiling constituents, removal of gasoline or desired hydrocarbons, and return of the lean gas to the formation. The input and output wells are usually spaced to have the lean gas displace the rich gas while maintaining the reservoir pressure.

The vapor-liquid separation processes in the refining of petroleum seldom give phase changes which may be called "retrograde" since isothermal or isobaric changes at conditions beyond the critical temperature or critical pressure of the mixture are not usually encountered. However, the reversal in the effect of pressure upon isothermal vaporization or condensation processes and the reversal in the effect of temperature upon isobaric vaporization or condensation processes which cause retrograde condensation do influence phase behavior accompanying combined pressure and temperature changes. Even at temperatures considerably below the critical temperature of the mixture, the equilibrium constants for the less volatile constituents may go through a minimum value and rise considerably as the mixture passes isothermally from low pressure to the bubble point of the mixtures. Although no isothermal retrograde condensation can occur at this temperature, the rise of the constants for the less volatile constituents being offset by the decrease in the constants for the more volatile constituents, the relative vaporization tendencies are significantly different from those at low pressures.

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Fine Particle Suspensions in Organic Liquids

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The sedimentation volumes of glass spheres, 5 to 15 microns in diameter, were determined in water and in a series of organic liquids. The sedimentation volumes in the organic liquids are identical with that in water or approach this volume as a minimum, as the system is dried more and more intensively. Flocculation of the particles causes the increase from the minimum value. The presence of water dissolved in the liquid and adsorbed on the particles produces this flocculation. The interfacial tension of the organic liquid against water is indicative of the tendency towards flocculation and the difficulty with which the minimum value may be attained. In some cases the sedimentation volume is proportional to the water content of the organic liquid, and in others the liquid must be nearly saturated before flocculation will take place.

THE phenomena of sedimentation and agglomeration are of vital importance in many manufacturing processes, particularly to the paint and printing ink industries. Agglomeration of pigment particles affects settling and flow properties of the paint as well as such factors as gloss, permeability, and durability of the film. For example, the control of flocculation of dispersion is of utmost importance in the formulation of coating compositions. A high degree of dispersion of pigment particles gives improved flow and gloss which are desirable in certain enamels. Flocculation of pigment particles which induces false bodying or reduced flow in paints is desirable in flat wall and metal protective compositions to permit uniform and complete coverage of the surfaces with one coat. A high degree of dispersion results in a hard cake formation of the pigments on settling, which is difficult to redisperse. On the other hand, flocculated pigments settle to a soft cake which is easily redispersed. It is evident, therefore, that a compromise between the two extremes of flocculation and dispersion must be made in practice to formulate usable compositions.

A suspension such as a paint is a complex system consisting of a number of solid and liquid phases, and it is almost impossible to determine the effect of a single substance in the mixture. On the other hand, the behavior of glass spheres