traditional formulation, metal←olefin, is misleading in that it implies general validity. It is obvious, of course, that the problem discussed above is not only of fundamental significance but also of great practical importance for the selection and design of metal complexes as catalysts for the various reactions of olefins.

We conclude this brief account by noting that only some of the pertinent data could be discussed here and none of them in adequate detail. Even so, the discussion raised perhaps more questions than could be answered. One important result of our inquiry into the role of the covalent molecule—apparently the first of its kind—is that it points to the many properties which need be considered and the interdependence of these properties. The main result, however, is the discovery that the acidity or oxidizing power of the covalent molecule is the principal factor which, other things being equal or nearly so, determines the reversibility of the metal complex–gas reactions. The main limitation, inherent in the type of our inquiry, is the obvious fact that the "other things" are never exactly equal for different molecules, not even in the homologous series of ethylenes (Table III).

I thank my former and present co-workers, whose names appear in the references, for their experimental contributions to this study. This work has been supported by the National Institutes of Health (Grant No. HE-09678), the National Center for Air Pollution Control, Bureau of Disease Prevention and Environmental Control (Grant No. AP-00574), and acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

The Critical Locus Curve and the Phase Behavior of Mixtures

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The locus of the critical points of a system of mixtures defines the upper limit in temperature and pressure of the heterogenous region. It therefore exerts a great influence on the form of the phase diagram. By the determination of the critical locus curves of a series of binary systems composed of a common component with the members of an homologous series of compounds, the development of the phase diagram from the relatively simple to the more complex form is revealed. These changes are related to the size, shape, and difference in chemical family of the component molecules.

The critical point of a liquid, whether it be a single compound or a mixture, is a property of considerable practical as well as theoretical importance. This is because the critical point defines the temperature and pressure where the liquid and vapor phases have identical properties and is, therefore, a key point in the construction of the phase diagram as well as in the development of a theory of the liquid state. Also, for the engineer, a knowledge of the critical temperature and pressure makes possible, by van der Waals' theorem of corresponding states, the prediction of the thermodynamic properties of the compound when these properties have not been determined experimentally.

Evidence for the existence of a critical point was first presented in 1822 by de la Tour,[1] who observed that a liquid when heated in a hermetically sealed glass tube is reduced to vapor in a space from two to four times the original volume of the sample. However, it was not until the quantitative measurements of Andrews on carbon dioxide[2] that the nature of the transition was understood. Andrews was the first to apply the term "critical point" to the phenomenon associated with the liquid–vapor transition. The first reliable experimental investigation of the critical state of liquid mixtures began with the work of Kuenen,[3] who used a magnetic stirrer to establish equilibrium between the liquid and vapor as the sample, confined over mercury in narrow glass capillaries, was compressed and heated. Kuenen showed that, unless the sample was well stirred, the observations could not be reproduced. Interest in the critical region of a mixture in the period 1876–1914 was heightened by the theoretical and experimental studies of van der Waals and his associates at the Universities of Amsterdam and Leiden. After World War I research on the phase behavior of mixtures was superseded by an interest in the atomic structure of matter. More recently, the increased use of high pressures in the chemical and petroleum industries has emphasized the paucity of accurate P–V–T data on pure substances and mixtures and the need for a better understanding of the phase behavior of liquid mixtures above atmospheric pressure. This has led to a resurgence of interest in the

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(1) C. de la Tour, *Ann. Chim.*, (3) **21**, 127 (1822).

(2) (a) T. Andrews, *Phil. Trans.*, **159**, 575 (1869); (b) *Proc. Roy. Soc.* (London), **18**, 42 (1869).

(3) (a) J. P. Kuenen, *Commun. Phys. Lab. Univ. Leiden*, No. 4B, 7 (1892); (b) *Koninkl. Akad. Wetenschapp. Amsterdam, Versl. Van Vergrad.*, **1**, 15 (1892); (c) *ibid.*, **3**, 90 (1894); (d) *Arch. Neerl. Sci.*, (ii) **1**, 331 (1898).

subject, as indicated by the increase in the number of publications in both the technical and scientific journals.

This paper deals with the phase behavior in the liquid–vapor critical region of a mixture and summarizes briefly the results of recent experimental studies relating to the critical locus curve in the P–T–x space. The presentation is directed more toward a general understanding of phase behavior than to establishing quantitative relations.

The Critical Point and the Critical Locus Curve of a Mixture

The liquid–vapor critical point of a mixture is defined as the temperature and associated pressure at which the coexisting liquid and vapor phases have identical properties. Figure 1 shows the P–T border curve of a simple mixture which corresponds to the vapor-pressure curve of a pure liquid. AB is the bubble point curve, the point of initial vaporization when the pressure is reduced at constant temperature; EDCB is the dew curve, the point of initial condensation when the pressure is increased at constant temperature between E and D. The two curves meet in the critical point B. The intermediate curves which converge to point B represent curves of constant volume fraction of the liquid sample. C and D are the points of maximum pressure and maximum temperature on the P–T border curve and, together with B, are uniquely definable points for a given mixture.

Between the critical temperature T_B and the maximum temperature T_D the vapor, when compressed from a lower pressure, begins to condense at point F and the liquid volume increases relatively slowly until a maximum is reached at point G. With a further small increase in pressure, the liquid volume decreases rapidly and completely disappears when the pressure reaches point H. This phenomenon was observed by Cailletet[4] in the case of a mixture of carbon dioxide and air. It was carefully and thoroughly investigated by Kuenen[8] and shown to be common to all mixtures. Kuenen gave the name "retrograde condensation" to the phenomenon, the word "retrograde" referring to that part of the isothermal compression where the liquid phase is vaporized by an increase of pressure. The same phenomenon is observed if the mixture is heated at constant pressure between the critical pressure P_B and the maximum pressure P_C. To differentiate between the two, the former is known as isothermal retrograde condensation and the latter, isobaric retrograde condensation.

The explanation of this seemingly anomalous behavior of the mixture is as follows. If the sample in the vapor state is compressed isothermally at the critical temperature, the initial condensate is richer in the less volatile component than the vapor, but as the pressure increases, the compositions of the liquid and vapor phases approach one another until finally the two phases have the same composition and the same physical properties. When this happens, the sample exhibits an intense opalescence similar to that observed at the critical point of a pure substance. When the isothermal compression is carried out at higher temperatures, both the liquid and vapor phases increase in the concentration of the more volatile component. Eventually, however, the vapor becomes so depleted in the less volatile component that its critical temperatures becomes less than the temperature of the compression. Then, as the supercritical vapor is dissolved into the liquid, the liquid evaporates and the mixture again is in an homogeneous state.

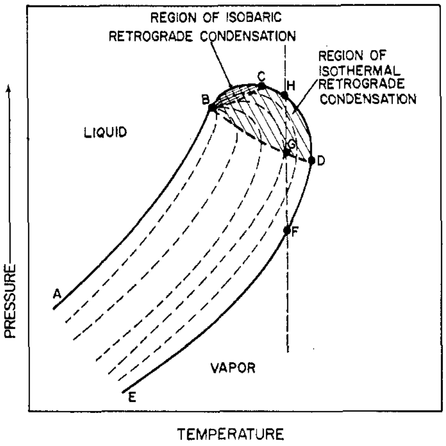

Figure 1. The P–T border curve of a mixture showing the region of retrograde condensation.

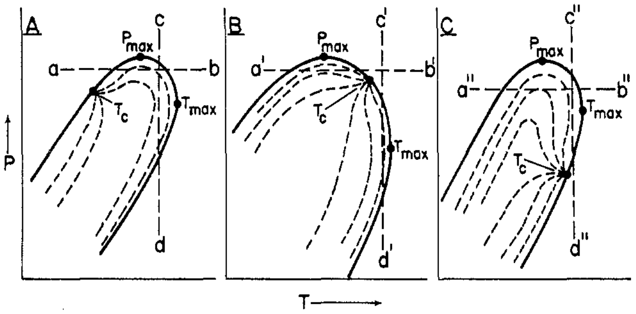

Figure 2. Kinds of retrograde condensation: (A) a–b, isobaric retrograde condensation, first kind; c–d, isothermal retrograde condensation, first kind; (B) a′–b′, isobaric retrograde condensation, second kind; d′–c′, isothermal retrograde condensation, first kind; (C) a″–b″, isobaric retrograde condensation, second kind; d″–c″, isothermal retrograde condensation, second kind.

At the maximum temperature T_D on the border curve a trace of liquid forms only at the corresponding pressure.

Kuenen[8] identified two kinds of retrograde condensation: the first kind is characterized by the transition vapor to vapor–liquid to vapor and the second by the transition liquid to liquid–vapor to liquid. Since these transitions may occur either isothermally or isobarically they are referred to respectively as isothermal retrograde condensation of the first or second kind, and isobaric retrograde condensation of the first or second kind. The differences between the two are shown in Figure 2. Isobaric retrograde condensation of the first kind and second kind and isothermal retrograde condensation of

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(4) L. Cailletet, *Compt. Rend.*, **90**, 210 (1880).

the first kind have been observed in many systems, whereas isothermal retrograde condensation of the second kind occurs only in mixtures that exhibit "gas-gas" equilibrium and possibly in those that form negative azeotropes.

When the vapor-pressure curves of the pure components and the P–T border curves for a series of their mixtures are plotted, a projection of the P–T–x space on a common P–T plane is obtained. Figure 3 is such a projection for the ethylene–n-heptane system.[5] Each border curve appears as the line of intersection of a plane of constant composition with the P–T–x space. The bubble point and dew point curves are respectively elements on the liquid and vapor surfaces that enclose a region where liquid and vapor coexist in equilibrium. The broken-line curve joining the critical points of the pure components and their mixtures is the critical locus curve of the system. Since it is tangent to the P–T border curves at the critical point of each mixture, it defines the upper limit of the liquid–vapor region. It is, therefore, a curve of major importance in the phase diagram of any mixture.

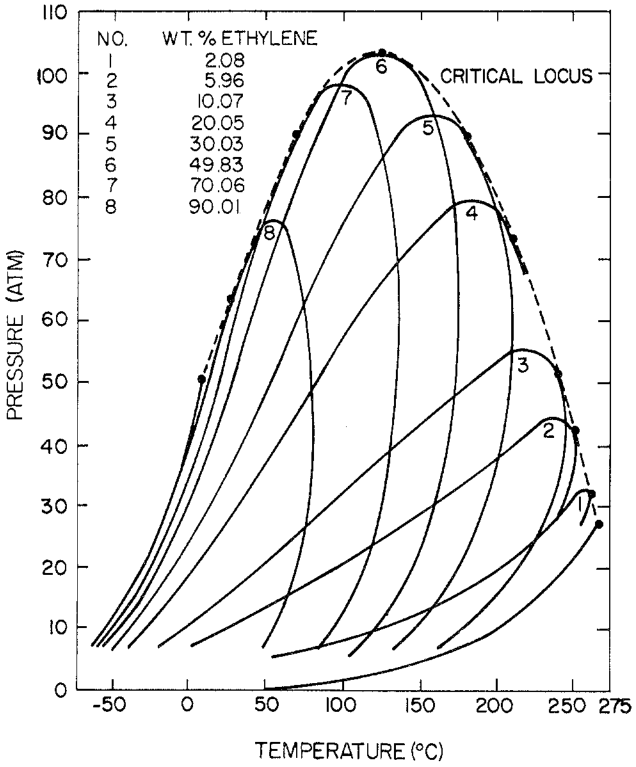

Figure 3. Projection of the P–T–x space of the system ethylene–n-heptane on the P–T plane.

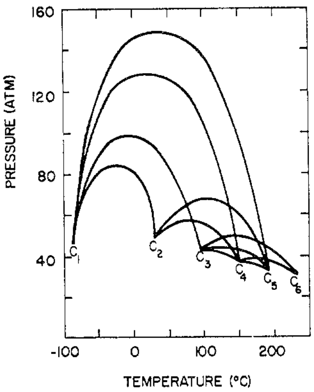

Figure 4. The effect of relative size of the components on the critical locus curves of binary systems of the n-alkanes.

The Shape of the Critical Locus Curve

The Relative Size of the Components. The shape of the critical locus curve depends in varying degrees on the relative size of the molecules, their molecular structure, and chemical nature or chemical family.[6] The relative size is defined as the ratio of the molecular weight of the less volatile to the more volatile compound. When the components of the mixture belong to the same chemical family, as for example, members of an homologous series, and are of about the same size, the critical locus curve approaches a straight line. As the relative size of the molecules increases, the straight line changes to a curved line, convex downward, and a maximum pressure point appears. With further increase in the relative size, the maximum pressure increases and may attain a very high value relative to the critical pressure of the pure components. Figure 4, which shows graphically the critical locus curves of binary systems of the n-alkanes between methane and n-hexane,[7] serves to illustrate these generalizations. It is to be noted that the lower members of the series exert a much greater influence on the critical locus curve than do the higher members. This is because the difference in the relative sizes of the component molecules in a series of systems with a common component changes more rapidly the lower the molecular weight of the common component.[8] In terms of methane as a common component, the relative sizes are: 1.9, 2.7, 3.6, and 4.5 in the methane binaries through n-pentane. The maximum critical pressures in these systems are approximately 85, 99.5, 131, and 151 atm, respectively. For the ethane series, the systems of corresponding relative size would be the binaries of n-butane, n-hexane, n-octane, and n-dode-

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(5) W. B. Kay, *Ind. Eng. Chem.*, **49**, 1459 (1948).

(6) The shape of the critical locus curve is ultimately the result of the sum total of the potential energies of interaction between the molecules. However, we do not have sufficient knowledge of how molecules interact to evaluate these potentials, and hence we choose size, shape, and chemical nature of the molecules as practical parameters to distinguish between the different types of phase behavior exhibited by mixtures in the vapor and liquid states.

(7) (a) O. T. Bloomer, D. C. Gami, and J. D. Parent, *Inst. Gas Technol. Res. Bull.*, No. 22 (1953); (b) C. N. Nysewander, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **32**, 118 (1940); **42**, 534 (1950); (c) B. H. Sage, B. L. Hicks, and W. N. Lacey, *ibid.*, **32**, 1085 (1940); (d) B. H. Sage, H. H. Reamer, R. H. Olds, and W. N. Lacey, *ibid.*, **34**, 1108 (1942); (e) W. B. Kay, *ibid.*, **32**, 353 (1940); (f) H. H. Reamer, B. H. Sage, and W. N. Lacey, *J. Chem. Eng. Data*, **5**, 44 (1960); (g) J. Barber, M.S. Thesis, The Ohio State University, 1964; (h) J. Oxley, M.S. Thesis, The Ohio State University, 1961; (i) D. Porthouse, M.S. Thesis, The Ohio State University, 1962; (j) R. Hoffman, M.S. Thesis, The Ohio State University, 1962; (k) O. Davies, M.S. Thesis, The Ohio State University, 1965.

(8) Systems of these compounds show positive deviations from Raoult's law as the difference in the molecular weights of the components increase. It might be expected, therefore, that the critical locus curve would possess a maximum point because the partial pressures of the components and, particularly, the more volatile components are greater than those predicted by Raoult's law.

cane. Unfortunately, the critical locus curves of these binaries have not been determined. However, for the binary systems methane–ethane, ethane–*n*-butane, propane–*n*-hexane, and *n*-butane–octane[9] whose molecular weight ratio varies from approximately 1.9 to 2.0, the maximum critical pressures are respectively 85, 57.4, 50, and 42.7 atm, which are much smaller than those for the methane series. A more meaningful basis for comparison of the maximum critical pressures of different systems is the difference between the absolute critical pressure and the pseudo-critical pressure.[10] On this basis, the comparable pressures for the above hydrocarbon binaries beginning with the ethane–*n*-butane system are respectively 12.3, 10.6, and 8.4 atm.

As a consequence of these relations, the critical locus curve of systems of hydrocarbons of high molecular weight but of about the same size should approach a straight line.

The work of Kohn[11] and Davenport and Rowlinson[12] indicates that a very definite change takes place in the locus curve as the differences in the physical properties increase with the size or chain length of the molecules. This change is manifested by the appearance of a second liquid layer in binary systems containing methane with *n*-hexane and higher homologs. With ethane as the common component immiscibility occurs only in systems of homologs containing more than 19 carbon atoms. For propane and *n*-butane, the incipient formation of a second liquid layer occurs in homologs of higher and higher molecular weight.

With the appearance of the second liquid layer the phase diagrams become more complex. Consider a mixture of A and B where A may be methane or ethane and B is a hydrocarbon of higher molecular weight that is not completely miscible with A. Figure 5, which represents graphically the *P–T* projection of the *P–T–x* space, serves to illustrate the phase behavior of such a mixture. AC_a and BC_b are the vapor-pressure curves of the pure components which terminate in their respective critical points, C_a and C_b. C_aO is the LG critical locus curve of mixtures rich in A that are miscible up to their LG critical point. D is the lower critical solution temperature (LCST), the temperature at which the system begins to separate into two liquid phases. DO is the three-phase line (L_AL_BG) that terminates in the critical end point O, where the A-rich liquid phase reaches its LG critical point. DE is an LL critical curve while EC_b is an LG critical curve since only one liquid phase exists above the temperature of the critical end point O. The pressures along the curve DEC_b are usually very high. Above the curve the system is homogeneous.

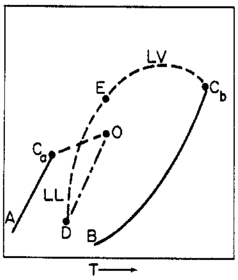

Figure 5. Limiting curves in the phase diagram of a binary system whose components A and B are partially miscible. Mixtures rich in A are completely miscible up to the critical point. Along DO, two liquid phases and a vapor phase coexist. At O the A-rich phase reaches its LG critical temperature. Beyond T_0, only liquid and vapor coexist.

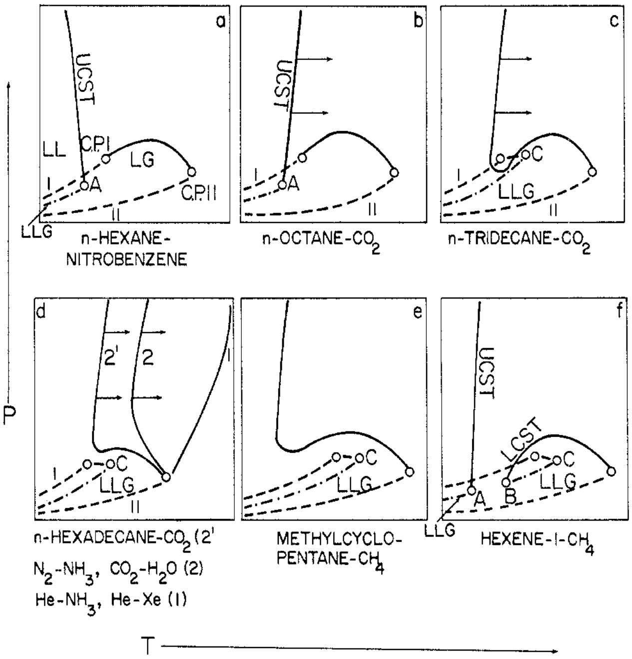

Figure 6. Development of the *P–T–x* phase diagram as the difference in the size, shape, and mutual solubilities of the components change: – – –, vapor-phase curve; –·–, three-phase curve; ————, critical locus curve. Diagram reproduced from G. Schneider, Meeting of the American Institute of Chemical Engineers, New York, N. Y., Nov 29, 1967, Paper 25a.

The diagram in Figure 5 will vary greatly depending on the properties and mutual solubilities of the components. Schneider[13] has illustrated this by schematic diagrams of different systems which are reproduced in Figure 6. In Figure 6a and 6b, both systems separate into two liquid layers at low temperature but reach an upper critical solution temperature (UCST) below the critical temperature of either component. They differ in that the UCST decreases with an increase in pressure in Figure 6a and increases with increase in pressure in Figure 6b. In the latter the mixture would separate into two liquid phases at a temperature greater than T_A if the pressure were increased sufficiently. In Figure 6c the UCST is slightly higher than the critical tem-

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(9) (a) See ref 7a; (b) W. B. Kay, *Ind. Eng. Chem.*, **32**, 358 (1940); (c) see ref 7i; (d) D. Fichtner, M.S. Thesis, The Ohio State University, 1964.

(10) W. B. Kay, *Ind. Eng. Chem.*, **28**, 1014 (1936).

(11) J. P. Kohn, *Am. Inst. Chem. Eng. J.*, **7**, 514 (1961).

(12) A. J. Davenport and J. S. Rowlinson, *Trans. Faraday Soc.*, **59**, 78 (1963). For the methane–*n*-hexane system, the lower critical solution temperature (LCST) was −90.7° for a mixture of 92.8 mole % methane. The pressure was not determined.

(13) G. Schneider, Meeting of the American Institute of Chemical Engineers, New York, N. Y., Nov 29, 1967, Paper 25a.

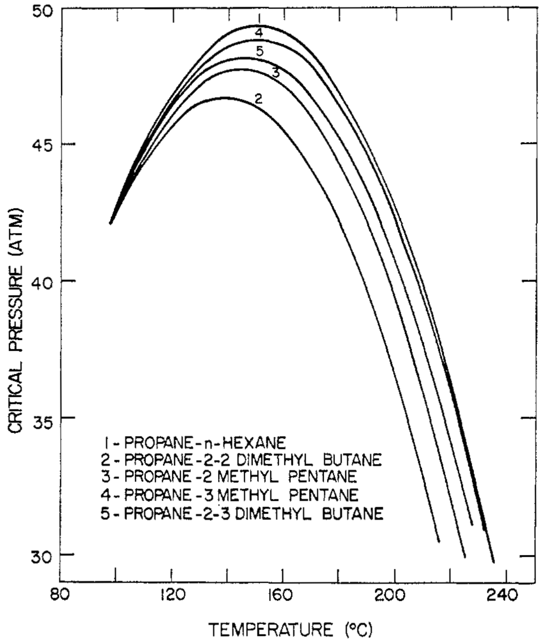

Figure 7. The effect of the shape of the molecules on the critical locus curve of propane–isomeric hexane systems. Note that the difference in the maximum pressure point is greatest between *n*-hexane and 2,2-dimethylbutane.

perature of component I and the LG critical locus curve merges in a continuous manner with the LL critical locus curve. Figure 6d shows the displacement of the critical locus curve to higher temperatures as the mutual solubility decreases and illustrates various stages in the development of the phase diagram as the difference in chain length of the molecules increases. For a system having a critical locus curve (Figure 6d-1), the critical temperature of a mixture would be higher than the critical temperature of either component. Isothermal retrograde condensation of the second kind would occur and the system would exhibit what has been erroneously called "gas–gas" equilibrium. Between point C and the critical point of the more volatile component in Figure 6e, mixtures rich in component I are miscible. Along the curve terminating in the critical end point C two liquid phases coexist. At pressures immediately above the curve the system is composed of two liquid phases. As the pressure increases, one of the liquid phases diminishes, and disappears when the pressure is above the critical locus curve. Figure 6f is illustrative of a system exhibiting partial miscibility in two separate temperature regions.

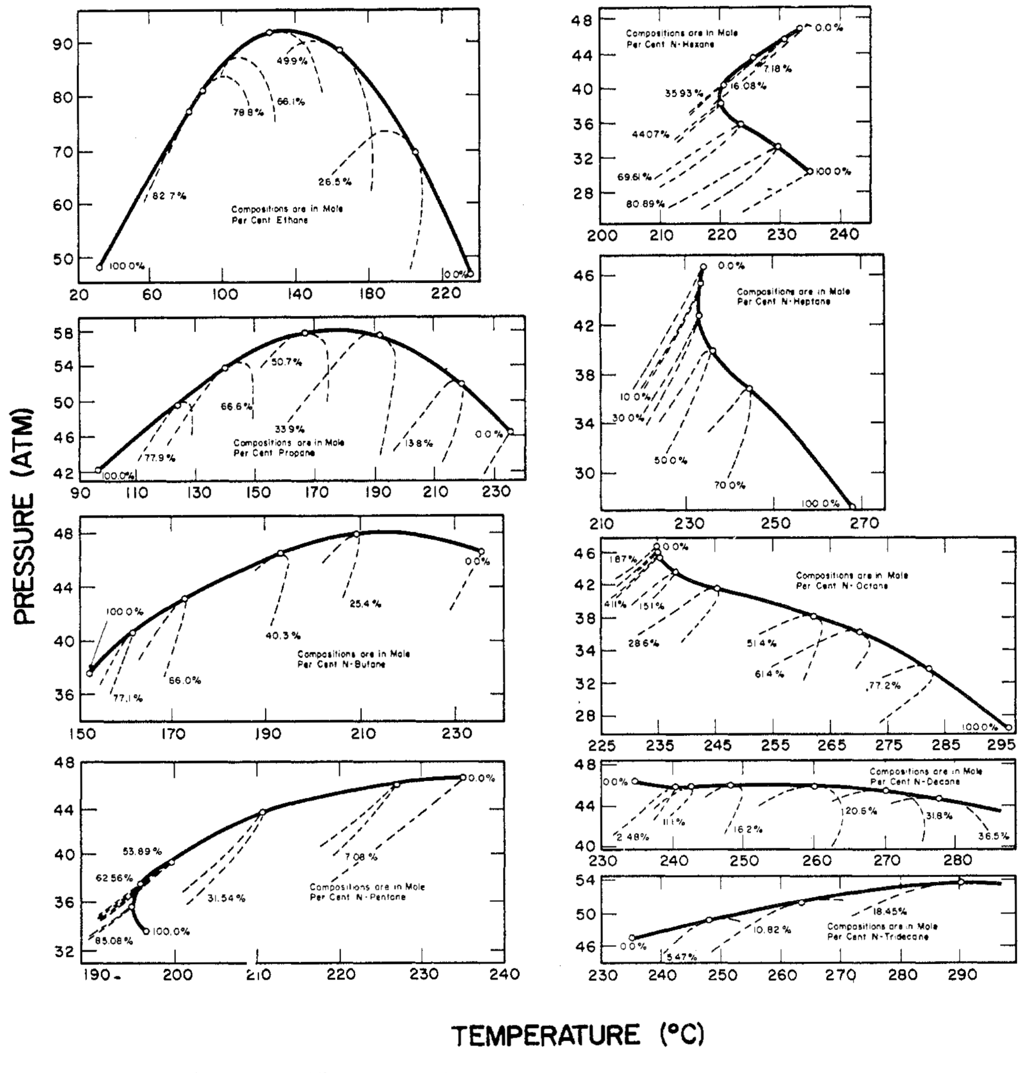

Figure 8. Pattern of phase behavior as the differences in the size of the component molecules constantly change in acetone–*n*-alkane systems.

The diagrams in Figures 4 and 5 are representative of the phase behavior in the critical region that would be expected in binary systems composed of a common component with the higher members of an homologous series.

Molecular Structure. Another variable that conceivably can affect the shape of the critical locus curve is the molecular structure. Undoubtedly, mixtures of molecules of different structure pack differently than molecules of the same structure, and this could result in different values of the critical temperature and pressure. Figure 7 shows the curves for the binaries of propane with the isomeric hexanes.[14] All the curves possess points of maximum pressure with the values of the pressure different for each system, thus furnishing evidence that molecular structure has an effect.

At present, the relation between molecular structure and properties is only empirical. An interesting correlation that may have an application to the problem here is that suggested by Wiener[15] for relating the standard boiling point of the isomers of the paraffin hydrocarbons to their molecular structure. To characterize isomeric compounds, two independent structural variables, the polarity number p and the path number w, were proposed. The polarity number is defined as the number of pairs of carbon atoms which are separated by three carbon–carbon bonds, while the path number is the sum of the distances between any two carbon atoms in the molecule in terms of the carbon–carbon bonds. In the application, Wiener related the difference between the boiling point of the normal compound and the boiling point of the branched-chain compound with the molecular structure. Stiel and Thodos[16] and McMicking and Kay[17] have shown that Wiener's polarity number and path number can be used to correlate satisfactorily the critical temperatures and pressures of the paraffin hydrocarbon isomers.

Chemical Nature of the Components. When components belonging to different chemical families are mixed, the greatest diversity in the shape of the critical locus curve would be expected. Figure 8, which shows the P–T projection of the P–T–x space of the acetone–n-alkane binaries,[18] is illustrative of the effect of differences in the chemical nature of the components. Starting with the ethane–acetone system, the critical locus curve possesses a point of maximum pressure whose absolute value is relatively much higher than the critical pressures of pure ethane and acetone. As the molecular weight of the hydrocarbon increases, the maximum pressure point decreases and disappears, and a minimum temperature point appears in the n-pentane–acetone system. The minimum temperature point persists in the n-hexane and n-heptane systems and then disappears; this is followed by the return of the maximum pressure point in the tridecane–acetone system.

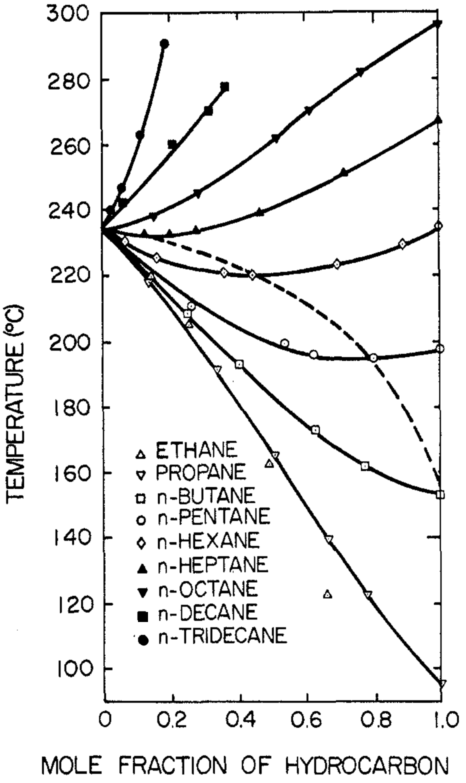

Figure 9. Critical temperature–composition relationships in the acetone–n-alkane systems. Binary systems that lie within the "azeotropic range" are acetone–n-butane through acetone–n-heptane.

The relations between the critical temperature and the composition are shown in Figure 9. The broken-line curve is the locus of the minimum critical temperature points. Only those systems whose critical temperatures lie within a given range of each other possess a point of minimum temperature. Since the latter is identified with systems that form azeotropes, this critical temperature range has been termed the critical "azeotropic range."[19] The azeotropic range of the n-alkane–acetone systems is approximately 160–270°. Only the critical temperatures of n-pentane, n-hexane, and possibly n-heptane fall within this range. The critical pressures of all systems in Figure 10 whose critical temperatures fall within the azeotropic range lie between the critical pressures of the pure components. Outside of this range the critical pressure–composition curves possess a point of maximum pressure. Similar relationships have been found for the following systems: acetic acid–n-alkanes and pyridine–n-alkanes,[20] carbon dioxide–n-alkanes,[21,22] perfluoro-n-heptane–n-alkanes,[23]

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(14) S. Chun, Ph.D. Thesis, The Ohio State University, 1964.

(15) H. Wiener, *J. Am. Chem. Soc.*, **69**, 17 (1947).

(16) L. I. Stiel and G. Thodos, *Am. Inst. Chem. Eng. J.*, **8**, 527 (1962).

(17) J. H. McMicking and W. B. Kay, *Proc. Am. Petrol. Inst., Sect. III*, **45**, No. 3, 75 (1965).

(18) W. B. Kay, *J. Phys. Chem.*, **68**, 827 (1964).

(19) A. Kreglewski, *Bull. Acad. Polon. Sci., Ser. Sci. Math. Astrom. Phys.*, **5**, 323 (1957).

(20) (a) A. Kreglewski, *ibid.*, **5**, 329 (1957); (b) *Roczniki Chem.*, **31**, 1001 (1957).

(21) F. Poettmann and D. Katz, *Ind. Eng. Chem.*, **37**, 849 (1945).

(22) G. Schneider, Z. Alwani, W. Heim, E. Horvath, and E. U. Franck, *Chem.-Ing.-Tech.*, **39**, 649 (1967).

(23) L. W. Jordan and W. B. Kay, *Chem. Eng. Progr. Symp. Ser.*, **59, No. 44,** 46 (1963).

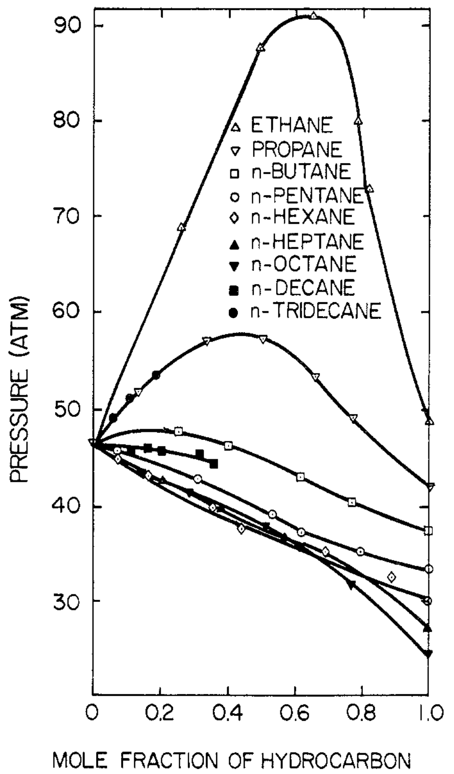

Figure 10. Critical pressure–composition relationships in the acetone–*n*-alkane systems. The point of maximum pressure is absent in those systems that lie within the "azeotropic range."

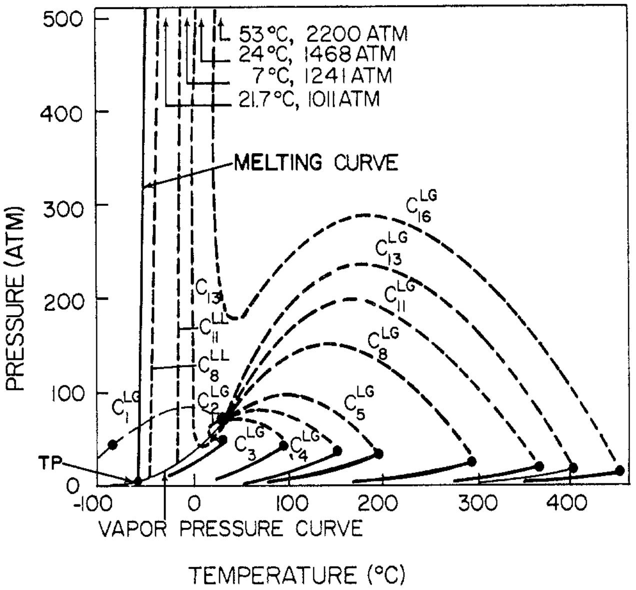

Figure 11. Continuous variation of the critical locus curve as the relative size of the components increases and their solubilities decrease: ———, vapor-pressure curves of pure components and melting curve of carbon dioxide; – – –, LG critical curves and LL curves; TP, triple point of carbon dioxide; ●, critical point of components; carbon dioxide–*n*-alkane systems. Diagram reproduced from G. Schneider, Z. Alwani, W. Heim, E. Horvath, and E. U. Franck, *Chem.-Ing.-Tech.*, **39**, 649 (1967).

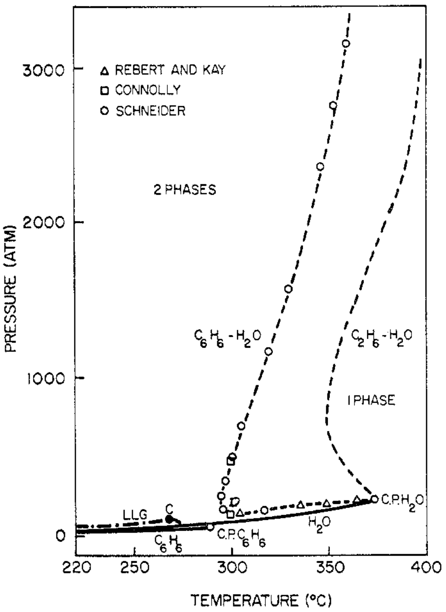

Figure 12. Critical locus curves of the benzene–water and ethane–water systems: ———, vapor-pressure curves of benzene and water; –·–, three-phase curve; – – –, LG critical locus; C, critical end point; CP, critical point. Diagram reproduced from Z. Alwani and G. Schneider, *Ber. Bunsenges. Phys. Chem.*, **71**, 633 (1967).

and benzene–*n*-alkyl alcohols.[24]

The greatest deviations from this pattern may be expected when the critical pressures of the components differ greatly. For example, if the homolog has a critical pressure much lower than that of the common component but the critical temperature is within the azeotropic range, a critical azeotrope may form without a minimum temperature point in the critical locus curve. Such conditions exist in the ethane–hydrogen sulfide system.[25] Also, when the critical temperature of the homolog falls just within the azeotropic range, the critical locus may exhibit a minimum temperature point, a minimum pressure point, and a maximum pressure point, as in the case of the ammonia–isooctane system.[26]

The recent work of Schneider and associates on the phase behavior of binary systems of carbon dioxide with the *n*-alkanes *n*-octane, *n*-undecane, *n*-tridecane, and *n*-hexadecane[22] has added much to our understanding of how the phase diagrams change as the relative size of the molecules increases. Figure 11 shows the *P–T* liquid–liquid and liquid–vapor critical locus curves for these systems as well as for those with methane,[27] ethane,[28] propane, *n*-butane, and *n*-pentane.[21] In the systems containing methane through *n*-tetradecane, the pattern of phase behavior is similar in all respects to that observed in the acetone–*n*-alkane series. The LG critical locus curves are continuous from the critical point of the pure hydrocarbon to the critical point of carbon dioxide. As the molecular weight of the hydrocarbon increases, its solubility in liquid carbon dioxide

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(24) J. M. Skaates and W. B. Kay, *Chem. Eng. Sci.*, **19**, 431 (1964).
(25) W. B. Kay and D. B. Brice, *Ind. Eng. Chem.*, **45**, 615 (1953).
(26) W. B. Kay and F. M. Warzel, *Am. Inst. Chem. Eng. J.*, **4**, 296 (1958).
(27) H. G. Donnelly and D. Katz, *Ind. Eng. Chem.*, **46**, 511 (1954).
(28) J. P. Kuenen, *Z. Physik. Chem.*, **24**, 667 (1897).

decreases, and the LCST increases, until the LG critical locus curve no longer ends in the critical point of carbon dioxide but merges with the LL critical curve, as shown for *n*-hexadecane.

The phase behavior of the benzene–water system is illustrative of still different changes in the shape of the critical locus curve. The system was studied at low pressure (up to 200 atm) by Rebert and Kay[29] and Connolly[30] and at high pressure by Alwani and Schneider.[31] Figure 12 is the *P–T* projection of the phase diagram. The LG critical locus curve is discontinuous and exists only for mixtures containing up to 25.8 wt % water and for mixtures containing over 92.8 wt % water. In the benzene-rich region it terminates in the critical end point C, while in the water-rich region it merges with the LL critical locus curve at D which extends upward and with a positive slope, to pressures of 3600 atm. The region between the critical end point C and point D is known as the miscibility gap.

Alwani and Schneider[31] suggest that the *P–T* locus curve, such as that for the benzene–water system and other binary systems of organic liquids and water, develops from a critical locus curve that possesses a point of minimum temperature, depending on the degree of mutual solubility of the two components. The diagrams in Figure 13 illustrate the transition. The dotted curves in Figure 13b and 13d do not exist. This region is the miscibility gap.

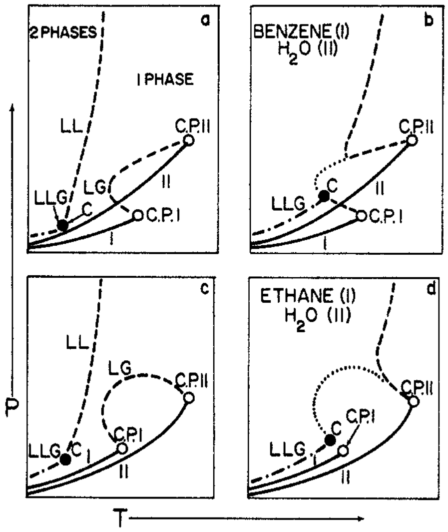

Figure 13. Schematic diagram to explain the development of the benzene–water and ethane–water phase diagrams. Diagram reproduced from Z. Alwani and G. Schneider, *Ber. Bunsenges. Phys. Chem.*, **71**, 633 (1967).

The determination of the critical locus curves of systems composed of an homologous series of compounds with a common component offer interesting possibilities in getting at the nature of the interactions between like and unlike molecules in the dense phase.

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