Equilibrium Ratios of Hydrogen and the Critical Loci of Hydrogen-paraffin Mixtures

This paper presents a correlation to predict the equilibrium ratios of hydrogen in hydrocarbon mixtures by use of the parameters of pressure and convergence pressure. Also a procedure to predict convergence pressures of hydrogen-containing mixtures was developed from a correlation of critical loci. With the predicted convergence pressure the measured values of hydrogen equilibrium ratios in binary hydrogen-paraffin mixtures were predicted with a statistical deviation of 8.1% for 237 measurements. Including hydrogen-olefin and multicomponent mixtures of hydrogen, paraffins, and olefins, the statistical deviation was found to be 11.3% for a total of 375 comparisons with measured values of hydrogen equilibrium ratios.

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With the increased use of catalytic cracking and catalytic reforming, mixtures of hydrogen and hydrocarbons are more and more commonly encountered. Often the phase behavior of such mixtures must be predicted under fairly high pressures. The prediction of the equilibrium ratios of hydrogen itself is important. In addition, the presence of hydrogen has a large effect on the critical locus of the system and appreciably influences the equilibrium ratios of the hydrocarbons. For liquid phases that are primarily paraffin hydrocarbons this paper presents a correlation to predict equilibrium ratios and convergence pressures for hydrogen containing mixtures. The development is based on published experimental measurements of equilibrium ratios and critical loci (*1, 2, 3, 4, 9, 11, 14, 17*).

METHOD OF CORRELATION

For hydrocarbons equilibrium ratios have been correlated by the use of convergence pressure Pg (*6, 10, 13, 15, 16, 18*), which is the isothermal projection to the critical locus of the binary mixture and is defined by the identity of the two binary components and the temperature. For a multicomponent mixture the convergence pressure may be determined by the isothermal projection to an equivalent binary critical locus (*6*) identified in general by hypothetical components (*10*). Mathematically, the equilibrium ratio $K = y/x$ is dependent upon four parameters,

$$K = f(i, T, Pg, P) \qquad (1)$$

A study of the equilibrium ratios of light hydrocarbons shows that at high temperatures and constant convergence pressure the equilibrium ratios become independent of temperature (*10, 12*). This independence of temperature as a variable begins at about 2.3 times the critical temperature of the component. Figure 1 illustrates this for methane, ethylene, and ethane. On the basis that this is a general relation, at constant convergence pressure the equilibrium ratios of hydrogen are essentially independent of temperature at temperatures above −300°F. The equilibrium-ratio relation for hydrogen reduces to

$$K = f(P, Pg) \qquad (2)$$

This equation has been used to prepare a chart for the prediction of hydrogen equilibrium ratios.

With the experimental data a series of plots was prepared of the equilibrium ratios of hydrogen as a function of pressure. Figure 2 illustrates the results for hydrogen in propane (*3, 17*). Other plots were made for hydrogen in methane (*2, 11*), ethane (*17*), *i*-butane (*4*), butane (*1*), trimethylpentane (*4*), and dodecane (*4*). On Figure 2, where the four lowest curves intersect the $K = 1$ line, the convergence pressures are directly established as 1,580, 3,430, 7,880, and 10,000 lb./sq. in. abs. Two methods can be used to establish the convergence pressure for the curves that do not cross $K = 1$ at pressures below 10,000 lb./sq. in. abs. Convergence pressures can be approximated by extrapolation to the $K = 1$ line if similitude to the shapes of the identified curves is used. By this method, for example, the curve labeled −150°F. gas a convergence pressure of 50,000 ± 20,000 lb./sq. in. abs. A better procedure is to plot identified convergence pressures against the equilibrium ratio at constant pressure on logarithmic graph paper, as illustrated on Figure 3. Such plots are straight lines if none of the curved portions of Figure 2 are included. By extrapolation of the straight lines of Figure 3, convergence-pressure identities above 10,000 lb./sq. in. abs. were estimated. With convergence-pressure identities for all experimental log K vs. log P plots, Figure 4 was developed by customary cross-plotting techniques. The chart shows hydrogen equilibrium ratios in paraffinic mixtures as a function of pressure and convergence pressure and is based upon measurements at temperatures from −200° to 303°F.

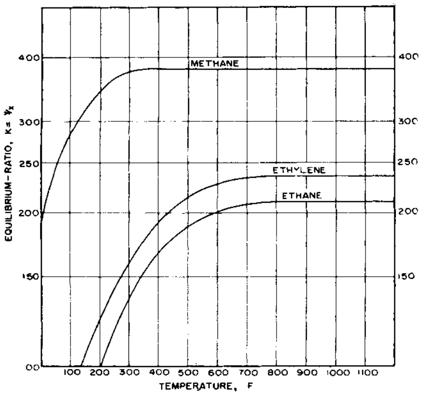

Fig. 1. Equilibrium ratios at 10 lb./sq. in. abs., constant convergence pressure of 5,000 lb./sq. in. abs.

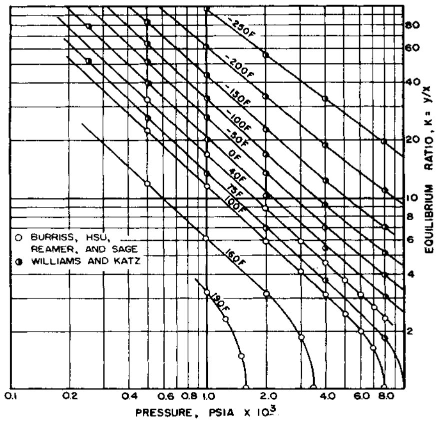

Fig. 2. Hydrogen equilibrium ratios in propane.

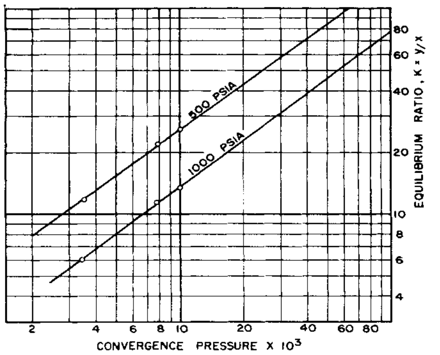

Fig. 3. Equilibrium ratios vs. convergence pressure.

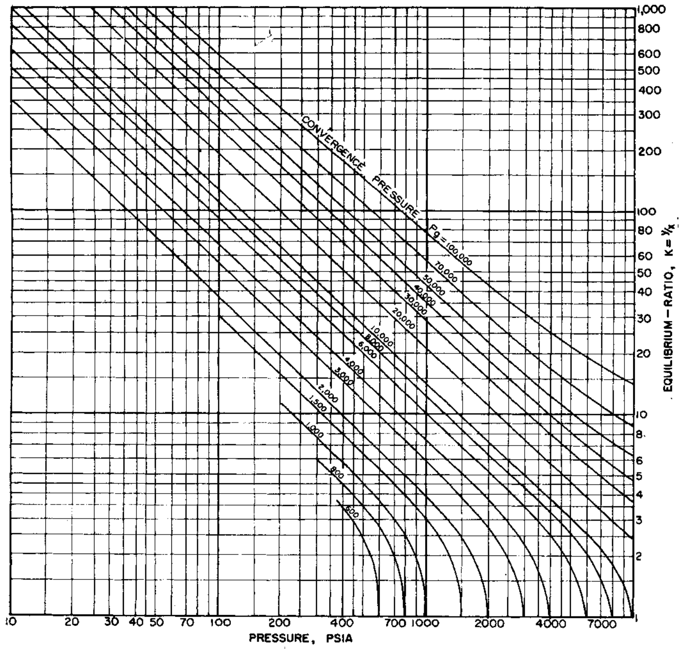

Fig. 4. Equilibrium ratios of hydrogen.

Table 1. Comparison of Experimental and Predicted Hydrogen Equilibrium Ratios
Binary Mixtures

Heavy component	Reference	Temp. °F.	Pressure, lb./sq. in. abs.	Predicted K	Measured K	Deviation, %
Methane	11	−175	630	11.7	11.5	1.7
Ethane	17	50	2,500	2.10	2.14	−1.6
Propane	3	40	2,500	6.6	7.09	−7.0
Butane	1	75	1,130	16.1	15.4	4.5
i-Butane	4	250	1,500	2.5	2.61	−4.2
Heptane	9	77	735	27	28.8	−6.2
Octane	9	122	735	24	25.3	−5.1
Trimethylpentane	4	100	175	103	110	−6.4
Dodecane	4	300	1,021	13.0	12.6	3.2

Table 2. Comparison of Experimental and Predicted Hydrogen Equilibrium Ratios
Ternary and Multicomponent Systems (*2*, *17*)

Temp., °F.	Pressure, lb./sq. in. abs.	x_{H_2}	EBP_L	EBP_H	Pg predicted	K predicted	K measured	Deviation, %
Hydrogen-ethylene-ethane								
−100	1,000	4.1	−393	−139	22,000	23.1	22.4	3.1
−100	8,000	30.7	−393	−140	22,000	3.1	3.03	2.3
Hydrogen-ethylene-propane								
−100	1,000	3.1	−393	−83	32,000	28.2	30.1	−6.3
−100	8,000	21.7	−393	−80	32,000	4.45	4.38	1.6
Hydrogen-propylene-propane								
−100	1,000	2.8	−393	−50	37,000	34.0	35.4	−4.0
−100	8,000	18.1	−393	−50	37,000	5.2	5.47	−4.9
Hydrogen-methane-propylene								
−100	500	0.728	−376	−98	12,200	26	20.6	26.2
−100	500	1.36	−393	−54	35,500	62	72.5	−14.5
Hydrogen-methane-propane								
0	500	0.329	−375	−59	7,500	23	23.1	−0.4
−200	1,000	1.79	−393	−53	74,000	60	55.3	8.5
Hydrogen, methane, ethylene, ethane, propylene, propane								
0	500	1.04	−391	−59	15,500	36	36.8	−2.2
−100	500	1.34	−389	−64	27,700	50	49.1	1.8

CRITICAL LOCI

With the curves of Figure 4, and experimental values of equilibrium ratios, the convergence pressures for the hydrogen-paraffin mixtures were determined for various temperatures. Figure 5 shows convergence pressures for various systems of hydrogen in paraffins ranging from methane to dodecane. Figure 5 is also a plot of critical-pressure loci, since the convergence- and critical-pressure loci are identical for binary systems. Figure 6, which shows the results of cross plotting Figure 5 with the boiling point of the paraffin hydrocarbon as a correlating parameter, is the correlation prepared for predicting convergence pressure of hydrocarbon mixtures containing hydrogen.

EXAMPLE

A liquid mixture of 0.062 mole fraction hydrogen and 0.938 mole fraction propane is at the bubble point at 100°F. and 1,000 lb./sq. in. abs. The boiling point of propane is −44°F. From Figure 6 the predicted convergence pressure is 7,800 lb./sq. in. abs. From Figure 4 the equilibrium ratio for hydrogen is 11.9. Burriss, Hsu, Reamer, and Sage (*3*) measured a convergence pressure of 7,880 lb./sq. in. abs. and an equilibrium ratio of 11.57.

PREDICTION ACCURACY

Table 1* illustrates the accuracy of prediction compared with experimentally measured values of equilibrium ratios in binary hydrogen-paraffin mixtures. Figures 4 and 6 predict the measured equilibrium ratios with an average arithmetic deviation of 5.9%, a trend of 0.7%, and a statistical deviation (root mean square) of 8.1%, by means of 237 measured values of equilibrium ratios. If the accuracy study is confined to convergence-pressure values over 40,000 lb./sq. in. abs., for twenty-four data points of binary hydrogen-paraffin mixtures the arithmetic-prediction deviation from the experimental values is 6.1% with an 8.1% statistical deviation, an indication that the extrapolation procedure used to identify the high convergence-pressure lines is reasonably satisfactory.

Williams and Katz (*17*) and Likhter and Tikhonovich (*11*) have measured hydrogen equilibrium ratios in binary mixtures of hydrogen with olefins. Figures 4 and 6 predict the experimental results of Williams and Katz for propylene, with an average deviation 12.7% low. For ethylene the predicted results average 14.7% higher than the measurements of Likhter and Tikhonovich, and 2.2% lower than the values of Williams and Katz. Although Figures 4 and 6 were developed for use with paraffins,

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*Tabular material has been deposited as document 5302 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

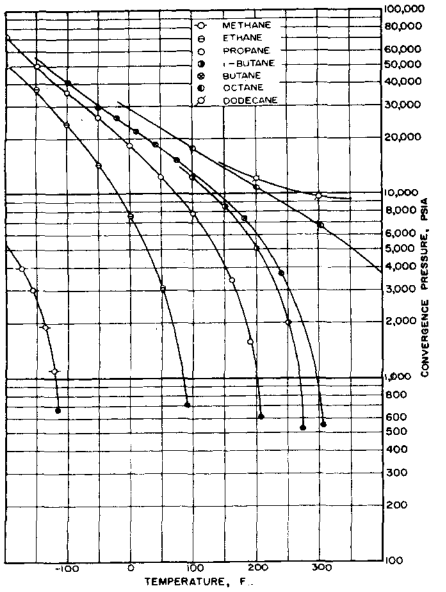

Fig. 5. Critical loci, hydrogen-paraffin mixtures.

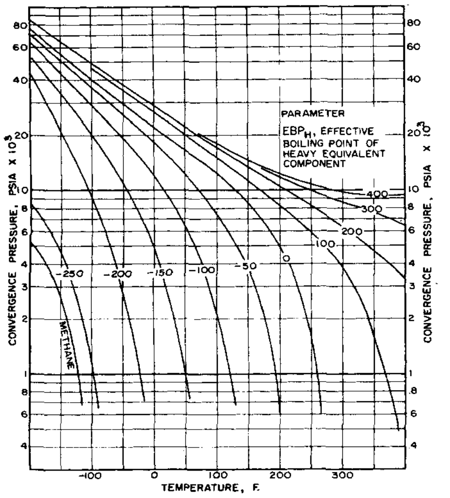

Fig. 6. Critical loci, hydrogen-paraffin mixtures.

they can be used with olefins with possibly somewhat poorer accuracy. The statistical deviation with olefin compounds is 14.2%.

Krichevskii and Efremova (*8*), who measured solubilities of hydrogen in benzene, derived hydrogen equilibrium ratios from these data that are 2.9 times larger than those predicted by Figures 4 and 6. The situation is similar with the hydrogen-benzene data of Gonikberg (*5*) and Inamvez and associates (*7*). Without correction it is unsafe to use this method for mixtures containing large amounts of aromatics.

MULTICOMPONENT SYSTEMS

Figures 4 and 6 are also useful in the prediction of hydrogen equilibrium ratios in multicomponent systems. The primary problem is to ascertain the mixture convergence pressure. This can be done by the use of the equivalent binary concept (*6, 10*). The identity of the two equivalent binary components may be described by their effective boiling points EBP_L and EBP_H and may be computed by a technique of averaging the component composition of the liquid phase (*10*). For ternary and multicomponent mixtures, Table 2 shows computed effective boiling points that identify the equivalent binary. For the systems listed in Table 2 it is safe to assume that the effective boiling point of the equivalent lighter component is the same as the EBP value, namely −393°F., of hydrogen itself when the hydrogen content of the liquid phase exceeds 1½%. The values of convergence pressure for systems where the value of EBP_L is greater than −393° are obtained by logarithmically averaging the convergence pressure obtained from Figure 6 and the convergence pressure with methane as the lighter component, obtained from the literature (*6, 10, 13, 16*). When these procedures are used to compute the equilibrium ratios in multicomponent systems, the predicted values deviate from the measured values by an arithmetic average of 11.3% and a statistical deviation of 17.7%. Over all, including binary, ternarys, and multicomponent mixtures, the average arithmetic prediction accuracy is 7.8%, with a statistical deviation of 11.3%, based on 375 measured values.

EFFECT OF HYDROGEN ON HYDROCARBON EQUILIBRIUM RATIOS

The addition of hydrogen to a hydrocarbon liquid phase results in a marked increase in the convergence pressure, with resulting modification of the equilibrium ratios. A small fraction of a mole per cent of hydrogen is often significant. The change in equilibrium ratios of the hydrocarbons can be corrected by the change in convergence pressure. With the correct convergence pressure established, the conventional prediction methods (*12, 13, 15, 16, 18*) may be used to predict the hydrocarbon equilibrium ratios, provided that the liquid phase is predominantly composed of hydrocarbons. Equilibrium ratios for systems where the liquid phase contains more than 10 mole % hydrogen cannot be safely predicted by these methods.

NORMAL BEHAVIOR

The equilibrium ratios of hydrogen have often been thought anomalous in their behavior because the equilibrium ratios decrease with increasing temperature. The reason for this is shown in Figure 6, which illustrates that as the temperature increases the convergence pressure decreases, with resulting decrease in equilibrium ratio. On the basis of the convergence-pressure concept, the behavior of the equilibrium ratios of hydrogen is conventional and fits in with the procedures for correlating hydrocarbon equilibrium ratios in a normal manner.

NOTATION

i = identity of a component

EBP_H = atmospheric-pressure boiling point of the hypothetical heavier component of the binary system having the same convergence pressure as the actual ternary or multicomponent system, F

EBP_L = The atmospheric-pressure boiling point of the hypothetical lighter component of the binary system having the same convergence pressure as the actual ternary or multicomponent system, F

K = equilibrium ratio, y/x

P = pressure, lb./sq. in. abs.

Pg = convergence pressure

T = temperature, °F.

y = mole fraction, vapor phase

x = mole fraction, liquid phase

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