# Volumetric and Phase Behavior in the Hydrogen–*n*-hexane System

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**In spite of the importance of hydrogenation processing operations in the refining of petroleum there are only limited experimental volumetric and phase equilibrium data concerning mixtures of hydrocarbons and hydrogen. An investigation of the volumetric and phase behavior of the hydrogen-*n*-hexane system was therefore undertaken.**

**The experimental study involved measurements of the specific volume of four mixtures of hydrogen and *n*-hexane at eight temperatures between 40° and 460°F. for pressures up to 10,000 lb./sq. in. In addition, the composition of the gas phase in heterogeneous mixtures was determined at six temperatures within the interval mentioned above for pressures as high as 10,000 lb./sq. in.**

**Little about this system was found to be qualitatively unusual except that the critical pressure exceeded 10,000 lb./sq. in. at all temperatures below 340°F. As would be expected, the dew-point gas was rather lean in *n*-hexane for temperatures below 220°F. and at pressures above 100 times the vapor pressure of *n*-hexane throughout the pressure range covered by this study.**

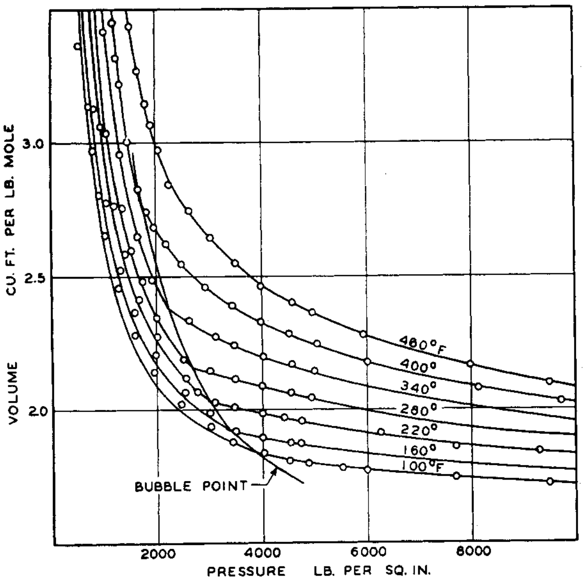

**Fig. 1. Sample experimental volumetric measurements for mixture containing 0.1895 mole fraction hydrogen.**

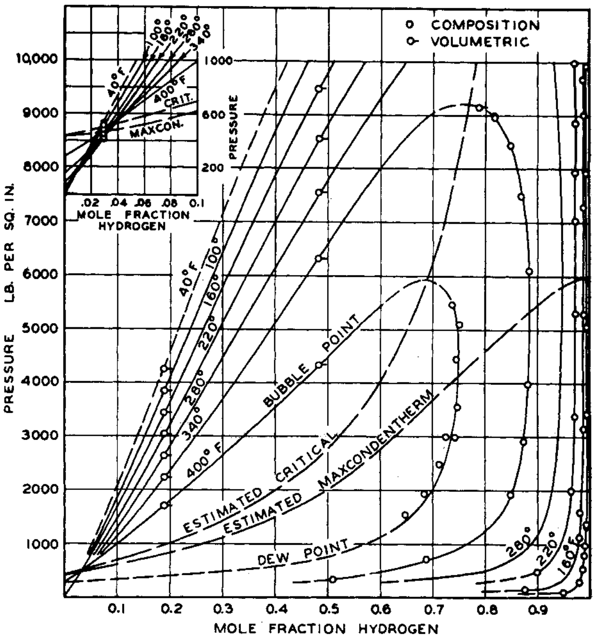

**Fig. 2. Composition of coexisting phases in hydrogen-*n*-hexane system.**

Only results from limited investigations of the volumetric and phase behavior of binary systems involving hydrogen and hydrocarbons at high pressures are available. The phase behavior of the hydrogen-propane system has been investigated (*2*) and the solubility of hydrogen has been determined in a number of hydrocarbons (*4*, *5*), but these limited data do not permit a general correlation of the effect of the characteristics of the hydrocarbon components upon the phase behavior of such systems or of the partial volume (*7*) of hydrogen in hydrocarbon liquids.

TABLE 1. MOLAL VOLUMES FOR MIXTURES OF HYDROGEN AND *n*-HEXANE

| Pressure lb./sq. in. | 40° F. | 100° F. | 160° F. | 220° F. | 280° F. | 340° F. | 400° F. | 460° F. |
|---|---|---|---|---|---|---|---|---|
| | | | | Mole fraction hydrogen = 0.1895 | | | | |
| Dew point | (9)* | (17) | (40) | (77) | (127) | (220) | (425) | |
| Bubble Point | (4,240)*<br>1.770 | (3,840)<br>1.844 | (3,430)<br>1.924 | (3,030)<br>2.030 | (2,640)<br>2.166 | (2,225)<br>2.381 | (1,705)<br>2.792 | |
| 200 | 6.78† | | | | | | | |
| 400 | 4.09 | 4.47 | 4.87 | 5.51 | 6.34 | | | |
| 600 | 3.25 | 3.40 | 3.65 | 4.05 | 4.59 | 5.30 | | |
| 800 | 2.758 | 2.920 | 3.10 | 3.40 | 3.72 | 4.20 | 4.96 | |
| 1,000 | 2.500 | 2.641 | 2.782 | 3.02 | 3.19 | 3.53 | 4.00 | 5.01 |
| 1,250 | 2.304 | 2.406 | 2.537 | 2.681 | 2.840 | 3.07 | 3.36 | 3.98 |
| 1,500 | 2.170 | 2.275 | 2.367 | 2.487 | 2.617 | 2.784 | 2.985 | 3.48 |

TABLE 1. (Cont.)

| Pressure lb./sq. in. | 40° F. | 100° F. | 160° F. | 220° F. | 280° F. | 340° F. | 400° F. | 460° F. |
|---|---|---|---|---|---|---|---|---|
| 1,750 | 2.080 | 2.170 | 2.260 | 2.363 | 2.458 | 2.607 | 2.778 | 3.20 |
| 2,000 | 2.010 | 2.092 | 2.168 | 2.256 | 2.352 | 2.473 | 2.679 | 3.01 |
| 2,250 | 1.960 | 2.034 | 2.109 | 2.185 | 2.267 | 2.382 | 2.605 | 2.879 |
| 2,500 | 1.919 | 1.985 | 2.052 | 2.128 | 2.200 | 2.347 | 2.542 | 2.790 |
| 2,750 | 1.885 | 1.946 | 2.007 | 2.076 | 2.163 | 2.319 | 2.493 | 2.714 |
| 3,000 | 1.861 | 1.918 | 1.973 | 2.037 | 2.148 | 2.289 | 2.451 | 2.649 |
| 3,500 | 1.820 | 1.870 | 1.917 | 2.008 | 2.114 | 2.240 | 2.384 | 2.548 |
| 4,000 | 1.788 | 1.833 | 1.893 | 1.984 | 2.084 | 2.200 | 2.330 | 2.472 |
| 4,500 | 1.762 | 1.808 | 1.877 | 1.966 | 2.063 | 2.166 | 2.283 | 2.416 |
| 5,000 | 1.756 | 1.791 | 1.859 | 1.946 | 2.039 | 2.135 | 2.244 | 2.365 |
| 6,000 | 1.737 | 1.770 | 1.833 | 1.909 | 1.992 | 2.082 | 2.174 | 2.275 |
| 7,000 | 1.722 | 1.756 | 1.812 | 1.886 | 1.954 | 2.039 | 2.124 | 2.214 |
| 8,000 | 1.706 | 1.742 | 1.796 | 1.861 | 1.931 | 2.006 | 2.084 | 2.162 |
| 9,000 | 1.693 | 1.726 | 1.778 | 1.844 | 1.910 | 1.980 | 2.049 | 2.117 |
| 10,000 | 1.678 | 1.711 | 1.764 | 1.828 | 1.892 | 1.954 | 2.021 | 2.077 |
| Mole fraction hydrogen = 0.4833 | | | | | | | | |
| Dew point | (34)* | (40) | (85) | (140) | (221) | (336) | (738) | |
| Bubble point | | | (9,500)*<br>1.424 | (8,575)<br>1.497 | (7,560)<br>1.597 | (6,320)<br>1.756 | (4,330)<br>2.193 | |
| 200 | | | | | | | | |
| 400 | | | | | | | | |
| 600 | | | | | | | | |
| 800 | 4.28† | 4.70 | | | | | | |
| 1,000 | 3.63 | 3.97 | 4.23 | 4.86 | | | | |
| 1,250 | 3.11 | 3.36 | 3.65 | 3.98 | 4.34 | 4.93 | | |
| 1,500 | 2.768 | 2.997 | 3.22 | 3.48 | 3.78 | 4.21 | 4.80 | |
| 1,750 | 2.522 | 2.724 | 2.913 | 3.13 | 3.37 | 3.73 | 4.15 | 4.75 |
| 2,000 | 2.341 | 2.517 | 2.678 | 2.863 | 3.08 | 3.36 | 3.74 | 4.20 |
| 2,250 | 2.202 | 2.361 | 2.506 | 2.670 | 2.857 | 3.09 | 3.39 | 3.72 |
| 2,500 | 2.091 | 2.226 | 2.361 | 2.513 | 2.678 | 2.879 | 3.12 | 3.41 |
| 2,750 | 1.996 | 2.127 | 2.250 | 2.384 | 2.531 | 2.707 | 2.912 | 3.18 |
| 3,000 | 1.923 | 2.041 | 2.150 | 2.278 | 2.411 | 2.562 | 2.740 | 2.997 |
| 3,500 | 1.800 | 1.901 | 2.004 | 2.108 | 2.222 | 2.343 | 2.471 | 2.698 |
| 4,000 | 1.716 | 1.800 | 1.898 | 1.981 | 2.077 | 2.181 | 2.286 | 2.483 |
| 4,500 | 1.641 | 1.733 | 1.804 | 1.889 | 1.963 | 2.052 | 2.152 | 2.324 |
| 5,000 | 1.585 | 1.662 | 1.738 | 1.806 | 1.874 | 1.948 | 2.050 | 2.202 |
| 6,000 | 1.506 | 1.565 | 1.627 | 1.683 | 1.738 | 1.796 | 1.903 | 2.026 |
| 7,000 | 1.443 | 1.497 | 1.549 | 1.595 | 1.642 | 1.702 | 1.801 | 1.903 |
| 8,000 | 1.397 | 1.442 | 1.486 | 1.528 | 1.567 | 1.638 | 1.724 | 1.814 |
| 9,000 | 1.348 | 1.399 | 1.437 | 1.475 | 1.519 | 1.590 | 1.665 | 1.744 |
| 10,000 | 1.338 | 1.367 | 1.396 | 1.433 | 1.485 | 1.558 | 1.619 | 1.683 |
| Mole fraction hydrogen = 0.7878 | | | | | | | | |
| Dew point | (61)* | (79) | (127) | (292) | (494) | | | |
| Bubble point | | | | | | | | |
| 200 | | | | | | | | |
| 400 | | | | | | | | |
| 600 | | | | | | | | |
| 800 | | | | | | | | |
| 1,000 | | | | | | | | |
| 1,250 | 3.95† | 4.35 | | | | | | |
| 1,500 | 3.38 | 3.74 | 4.09 | 4.49 | | | | |
| 1,750 | 2.977 | 3.28 | 3.60 | 3.92 | 4.30 | | | |
| 2,000 | 2.681 | 2.949 | 3.21 | 3.50 | 3.83 | 4.27 | | |
| 2,250 | 2.448 | 2.683 | 2.920 | 3.18 | 3.46 | 3.83 | 4.19 | 4.51 |
| 2,500 | 2.266 | 2.478 | 2.686 | 2.917 | 3.17 | 3.48 | 3.81 | 4.09 |
| 2,750 | 2.109 | 2.309 | 2.504 | 2.702 | 2.926 | 3.20 | 3.51 | 3.76 |
| 3,000 | 1.986 | 2.165 | 2.335 | 2.526 | 2.727 | 2.966 | 3.23 | 3.48 |
| 3,500 | 1.787 | 1.926 | 2.087 | 2.248 | 2.413 | 2.613 | 2.82 | 3.04 |
| 4,000 | 1.636 | 1.763 | 1.898 | 2.037 | 2.182 | 2.343 | 2.522 | 2.715 |
| 4,500 | 1.520 | 1.638 | 1.757 | 1.890 | 1.999 | 2.137 | 2.294 | 2.464 |
| 5,000 | 1.427 | 1.528 | 1.640 | 1.749 | 1.860 | 1.974 | 2.113 | 2.262 |
| 6,000 | 1.288 | 1.369 | 1.470 | 1.552 | 1.642 | 1.740 | 1.846 | 1.960 |
| 7,000 | 1.184 | 1.258 | 1.336 | 1.409 | 1.489 | 1.572 | 1.664 | 1.763 |
| 8,000 | 1.109 | 1.177 | 1.240 | 1.308 | 1.375 | 1.442 | 1.526 | 1.612 |
| 9,000 | 1.051 | 1.121 | 1.167 | 1.224 | 1.280 | 1.337 | 1.419 | 1.494 |
| 10,000 | 1.018 | 1.065 | 1.118 | 1.158 | 1.212 | 1.270 | 1.332 | 1.403 |

*Values in parentheses represent pressures expressed in pounds per square inch absolute.
†Volume expressed in cubic feet per pound mole.

In order to extend the knowledge of the volumetric and phase behavior of hydrogen-hydrocarbon systems, an experimental study of the hydrogen–*n*-hexane system was carried out at temperatures between 40° and 460°F. and for pressures up to 10,000 lb./sq. in. The investigation included a direct evaluation of the composition of the gas phase in heterogeneous mixtures of these components, as well as measurements of the specific volume of four mixtures as a function of pressure and temperature.

The volumetric behavior of hydrogen has been investigated in detail, but it is beyond the scope of the present discussion to present a review of these data. For present purposes the measurements of Wiebe and Gaddy (*15*) and Deming and Shupe (*3*) were employed. The latter data appeared to describe the volumetric behavior of hydrogen with an uncertainty of less than 0.2%. A recent study of the volumetric behavior of *n*-hexane (*14*) is in good agreement with the earlier measurements of Kelso and Felsing (*6*). Volumetric behavior of *n*-hexane in the liquid phase is known throughout the range of pressures and temperatures of interest with an uncertainty of approximately 0.25%. There is no experimental information available at higher than atmospheric pressure to describe the volumetric behavior of *n*-hexane in the gas phase, except for states at temperatures above 482°F., where some measurements are reported by Kelso and Felsing (*6*).

The foregoing experimental information concerning the volumetric behavior of hydrogen and *n*-hexane suffices for present needs and aids in the smoothing of the present data with respect to composition. The behavior of hydrogen and *n*-hexane is not reported here.

## METHODS AND APPARATUS

This investigation will determine specific volume as a function of pressure and temperature for a series of mixtures of hydrogen and *n*-hexane of chosen compositions. In principle the experimental methods involved the confinement of a sample mixture of known composition and weight in a stainless steel pressure vessel over mercury.

Effective volume of this chamber was varied by the introduction or withdrawal of mercury. Mechanical agitation was provided to hasten the attainment of physical equilibrium within and between the phases. The details of the experimental apparatus used for this purpose have been described (*13*). Pressures were measured by means of a balance utilizing a piston-cylinder combination (*13*), which was calibrated against the vapor pressure of carbon dioxide (*1*). Recent experience with such an instrument (*11*) indicates that the pressures within the apparatus relative to the vapor pressure of carbon dioxide at the ice point were known within 0.2 lb./sq. in. or 0.10%, whichever was the larger measure of uncertainty.

The stainless steel vessel containing the hydrocarbons under investigation was immersed in an agitated liquid bath, the temperature of which was controlled with a resistance thermometer through a modulating electronic circuit (*10*). This temperature was related to the international platinum scale by means of a strain-free platinum resistance thermometer of the coiled-filament type (*8*), which was compared with the indications of a similar instrument that had been calibrated by the National Bureau of Standards. The temperature of the contents of the pressure vessel was known within 0.02°F. of the international platinum scale throughout the temperature interval between 40° and 460°F.

The *n*-hexane was introduced by weighing-bomb techniques (*13*) and the hydrogen by volumetric methods involving a measured change in the volume in an auxiliary reservoir at constant pressure under isothermal conditions.

The weight of the mixtures was known within 0.05% for all four compositions investigated. Experience with the equipment indicates that the relative probable error in specific volume at pressures below 5,000 lb./sq. in. was approximately 0.25%. This probable error increased gradually at the higher pressure to a relative value of 0.5% at 10,000 lb./sq. in. The larger uncertainties at the higher pressures resulted from difficulties in obtaining reproducible calibrations of the volumetric equipment under these conditions.

Some difficulty was experienced from thermal rearrangement of the *n*-hexane at temperatures of 400° and 460°F., indicated by comparison of the equilibrium volumetric behavior near the bubble point for samples at 100°F. which had and had not been subjected to investigation at 400° and 460°F. An increase in bubble-point pressure of as much as 10 lb./sq. in. was experienced in the case of the mixtures rich in *n*-hexane. It therefore should be emphasized that in the vicinity of bubble point, measurements at 400° and 460°F. are subject to an additional uncertainty beyond that just described. However, this thermal rearrangement did not significantly modify the volumetric behavior in the condensed liquid or in the heterogeneous region at specific volumes several times the volume of bubble point. Some difficulty was experienced in obtaining molal volumes in the heterogeneous region with as small an uncertainty as would be estimated from the accuracy of the evaluation of the individual variables. This uncertainty apparently resulted from difficulties in attaining equilibrium between the phases in the heterogeneous region. For this reason it is probable that the molal volumes of the heterogeneous mixtures may involve uncertainties as large as 1%. These uncertainties are probably largest and most frequently encountered at the lower temperatures.

In order to establish the composition of the gas phase of heterogeneous mixtures of hydrogen and *n*-hexane, it was found desirable to determine the mole fraction of each of the components by direct measurement. It was not found desirable to utilize volumetric measurements at constant composition to obtain these data. The small change in composition which was experienced at dew point with large changes in pressure throughout the greater part of the temperature interval covered by this investigation renders measurements at constant composition ineffective.

As a result of the marked difference in

TABLE 2. PROPERTIES OF THE COEXISTING GAS AND LIQUID PHASES IN THE HYDROGEN–*n*-HEXANE SYSTEM

| Pressure, lb./sq. in. | Mole fraction hydrogen | Volume, cu. ft./lb. mole | Mole fraction hydrogen | Volume, cu. ft./lb. mole | Equilibrium ratio | |
|---|---|---|---|---|---|---|
| | Dew point | | Bubble point | | Hydrogen | *n*-Hexane |
| | | | 40° F. | | | |
| 1.107* | 0 | — | 0 | 2.064 | — | 1.0000 |
| 500 | 0.996 | — | 0.028 | 2.022 | 35.19 | 0.0041 |
| 1,000 | 0.998 | — | 0.054 | 1.980 | 18.53 | 0.0026 |
| 1,500 | 0.998 | 3.80† | 0.078 | 1.945 | 12.88 | 0.0023 |
| 2,000 | 0.998 | 2.914 | 0.099 | 1.912 | 10.04 | 0.0022 |
| 2,500 | 0.998 | 2.381 | 0.120 | 1.880 | 8.288 | 0.0023 |
| 3,000 | 0.998 | 2.023 | 0.140 | 1.850 | 7.103 | 0.0023 |
| 3,500 | 0.998 | 1.768 | 0.160 | 1.818 | 6.238 | 0.0024 |
| 4,000 | 0.998 | 1.577 | 0.179 | 1.790 | 5.562 | 0.0024 |
| 4,500 | 0.998 | 1.429 | 0.199 | 1.754 | 5.024 | 0.0025 |
| 5,000 | 0.998 | 1.311 | 0.218 | 1.721 | 4.588 | 0.0026 |
| 6,000 | 0.998 | 1.132 | 0.256 | 1.659 | 3.904 | 0.0027 |
| 7,000 | 0.998 | 1.007 | 0.294 | 1.598 | 3.391 | 0.0028 |
| 8,000 | 0.998 | 0.9150 | 0.334 | 1.531 | 2.988 | 0.0030 |
| 9,000 | 0.998 | 0.8449 | 0.376 | 1.472 | 2.654 | 0.0032 |
| 10,000 | 0.998 | 0.7920 | 0.422 | 1.414 | 2.365 | 0.0035 |
| | | | 100° F. | | | |
| 4.954* | 0 | — | 0 | 2.148 | — | 1.0000 |
| 500 | 0.986 | — | 0.031 | 2.095 | 31.81 | 0.0144 |
| 1,000 | 0.992 | — | 0.059 | 2.050 | 16.81 | 0.0085 |
| 1,500 | 0.994 | 4.24† | 0.084 | 2.015 | 11.83 | 0.0066 |
| 2,000 | 0.995 | 3.24 | 0.108 | 1.975 | 9.209 | 0.0061 |
| 2,500 | 0.995 | 2.643 | 0.131 | 1.940 | 7.595 | 0.0058 |
| 3,000 | 0.995 | 2.242 | 0.153 | 1.900 | 6.503 | 0.0061 |
| 3,500 | 0.995 | 1.958 | 0.175 | 1.870 | 5.686 | 0.0061 |
| 4,000 | 0.995 | 1.744 | 0.196 | 1.830 | 5.077 | 0.0062 |
| 4,500 | 0.995 | 1.578 | 0.217 | 1.800 | 4.585 | 0.0064 |
| 5,000 | 0.995 | 1.445 | 0.238 | 1.772 | 4.181 | 0.0066 |
| 6,000 | 0.995 | 1.245 | 0.279 | 1.698 | 3.566 | 0.0069 |
| 7,000 | 0.995 | 1.104 | 0.322 | 1.620 | 3.090 | 0.0074 |
| 8,000 | 0.995 | 1.000 | 0.366 | 1.545 | 2.719 | 0.0079 |
| 9,000 | 0.995 | 0.9221 | 0.412 | 1.461 | 2.415 | 0.0085 |
| 10,000 | 0.995 | 0.8607 | 0.461 | 1.390 | 2.158 | 0.0093 |
| | | | 160° F. | | | |
| 15.82* | 0 | — | 0 | 2.256 | — | 1.0000 |
| 500 | 0.961 | — | 0.034 | 2.195 | 28.69 | 0.0403 |
| 1,000 | 0.978 | — | 0.064 | 2.140 | 15.28 | 0.0235 |
| 1,500 | 0.983 | 4.66† | 0.092 | 2.090 | 10.68 | 0.0187 |
| 2,000 | 0.986 | 3.56 | 0.119 | 2.041 | 8.286 | 0.0159 |
| 2,500 | 0.987 | 2.902 | 0.144 | 2.000 | 6.854 | 0.0152 |
| 3,000 | 0.988 | 2.460 | 0.169 | 1.960 | 5.846 | 0.0144 |
| 3,500 | 0.988 | 2.147 | 0.193 | 1.920 | 5.119 | 0.0149 |
| 4,000 | 0.988 | 1.912 | 0.216 | 1.880 | 4.574 | 0.0153 |
| 4,500 | 0.988 | 1.728 | 0.239 | 1.840 | 4.134 | 0.0158 |
| 5,000 | 0.988 | 1.581 | 0.262 | 1.798 | 3.770 | 0.0163 |
| 6,000 | 0.988 | 1.359 | 0.309 | 1.710 | 3.197 | 0.0174 |
| 7,000 | 0.988 | 1.202 | 0.356 | 1.630 | 2.775 | 0.0186 |
| 8,000 | 0.988 | 1.084 | 0.405 | 1.543 | 2.440 | 0.0202 |
| 9,000 | 0.988 | 0.9968 | 0.456 | 1.460 | 2.167 | 0.0221 |
| 10,000 | 0.988 | 0.9290 | 0.511 | 1.380 | 1.933 | 0.0245 |

TABLE 2. (Cont.)

| Pressure, lb./sq. in. | Dew point | | Bubble point | | Equilibrium ratio | |
|---|---|---|---|---|---|---|
| | Mole fraction hydrogen | Volume, cu. ft./lb. mole | Mole fraction hydrogen | Volume, cu. ft./lb. mole | Hydrogen | *n*-Hexane |
| 220° F. | | | | | | |
| 39.87* | 0 | — | 0 | 2.391 | — | 1.0000 |
| 500 | 0.904 | — | 0.036 | 2.321 | 25.11 | 0.0996 |
| 1,000 | 0.946 | — | 0.070 | 2.256 | 13.51 | 0.0581 |
| 1,500 | 0.960 | 5.07† | 0.102 | 2.195 | 9.412 | 0.0445 |
| 2,000 | 0.966 | 3.87 | 0.132 | 2.137 | 7.318 | 0.0392 |
| 2,500 | 0.969 | 3.16 | 0.160 | 2.082 | 6.056 | 0.0369 |
| 3,000 | 0.971 | 2.677 | 0.187 | 2.032 | 5.193 | 0.0357 |
| 3,500 | 0.973 | 2.334 | 0.215 | 1.984 | 4.526 | 0.0344 |
| 4,000 | 0.974 | 2.078 | 0.241 | 1.931 | 4.041 | 0.0343 |
| 4,500 | 0.974 | 1.898 | 0.267 | 1.882 | 3.634 | 0.0355 |
| 5,000 | 0.974 | 1.718 | 0.293 | 1.835 | 3.324 | 0.0368 |
| 6,000 | 0.974 | 1.475 | 0.345 | 1.740 | 2.823 | 0.0397 |
| 7,000 | 0.974 | 1.300 | 0.396 | 1.648 | 2.460 | 0.0430 |
| 8,000 | 0.974 | 1.170 | 0.450 | 1.552 | 2.164 | 0.0473 |
| 9,000 | 0.974 | 1.070 | 0.508 | 1.448 | 1.917 | 0.0528 |
| 10,000 | 0.973 | 0.9990 | 0.570 | 1.347 | 1.707 | 0.0628 |
| 280° F. | | | | | | |
| 84.93* | 0 | — | 0 | 2.565 | — | 1.0000 |
| 500 | 0.797 | — | 0.038 | 2.489 | 20.97 | 0.2110 |
| 1,000 | 0.886 | — | 0.078 | 2.400 | 11.36 | 0.1236 |
| 1,500 | 0.914 | — | 0.115 | 2.321 | 7.948 | 0.0972 |
| 2,000 | 0.927 | 4.17† | 0.149 | 2.250 | 6.221 | 0.0858 |
| 2,500 | 0.934 | 3.40 | 0.181 | 2.185 | 5.160 | 0.0806 |
| 3,000 | 0.939 | 2.887 | 0.213 | 2.120 | 4.408 | 0.0775 |
| 3,500 | 0.942 | 2.520 | 0.244 | 2.060 | 3.861 | 0.0767 |
| 4,000 | 0.944 | 2.240 | 0.274 | 2.000 | 3.445 | 0.0771 |
| 4,500 | 0.945 | 2.025 | 0.304 | 1.940 | 3.109 | 0.0790 |
| 5,000 | 0.946 | 1.854 | 0.334 | 1.882 | 2.832 | 0.0811 |
| 6,000 | 0.946 | 1.595 | 0.393 | 1.765 | 2.407 | 0.0890 |
| 7,000 | 0.945 | 1.411 | 0.451 | 1.660 | 2.095 | 0.1002 |
| 8,000 | 0.944 | 1.270 | 0.511 | 1.545 | 1.847 | 0.1145 |
| 9,000 | 0.941 | 1.168 | 0.576 | 1.440 | 1.634 | 0.1392 |
| 10,000 | 0.931 | 1.095 | 0.649 | 1.332 | 1.435 | 0.1966 |
| 340° F. | | | | | | |
| 160.28* | 0 | — | 0 | 2.806 | — | 1.0000 |
| 500 | 0.606 | — | 0.037 | 2.726 | 16.22 | 0.4091 |
| 1,000 | 0.772 | — | 0.086 | 2.615 | 8.977 | 0.2495 |
| 1,500 | 0.826 | — | 0.132 | 2.510 | 6.258 | 0.2005 |
| 2,000 | 0.851 | 4.45† | 0.172 | 2.423 | 4.948 | 0.1800 |
| 2,500 | 0.865 | 3.63 | 0.210 | 2.340 | 4.119 | 0.1709 |
| 3,000 | 0.873 | 3.08 | 0.249 | 2.254 | 3.506 | 0.1691 |
| 3,500 | 0.878 | 2.690 | 0.285 | 2.170 | 3.081 | 0.1706 |
| 4,000 | 0.882 | 2.394 | 0.322 | 2.096 | 2.739 | 0.1740 |
| 4,500 | 0.884 | 2.166 | 0.359 | 2.020 | 2.462 | 0.1810 |
| 5,000 | 0.885 | 1.986 | 0.394 | 1.942 | 2.246 | 0.1898 |
| 6,000 | 0.884 | 1.720 | 0.461 | 1.800 | 1.918 | 0.2152 |
| 7,000 | 0.880 | 1.539 | 0.528 | 1.657 | 1.667 | 0.2542 |
| 8,000 | 0.865 | 1.410 | 0.597 | 1.522 | 1.449 | 0.3350 |
| 9,000 | 0.815 | 1.325 | 0.691 | 1.382 | 1.179 | 0.5987 |
| 9,200‡ | 0.768 | 1.333 | 0.768 | 1.333 | 1.000 | 1.0000 |
| 400° F. | | | | | | |
| 277.53* | 0 | — | 0 | 3.23 | — | 1.0000 |
| 500 | 0.310 | — | 0.032 | 3.15 | 9.688 | 0.7128 |
| 1,000 | 0.568 | — | 0.103 | 2.980 | 5.515 | 0.4816 |
| 1,500 | 0.656 | — | 0.165 | 2.840 | 3.967 | 0.4120 |
| 2,000 | 0.700 | 4.61† | 0.224 | 2.700 | 3.125 | 0.3866 |
| 2,500 | 0.722 | 3.78 | 0.283 | 2.581 | 2.551 | 0.3877 |
| 3,000 | 0.736 | 3.22 | 0.341 | 2.460 | 2.158 | 0.4006 |
| 3,500 | 0.745 | 3.82 | 0.396 | 2.355 | 1.881 | 0.4222 |
| 4,000 | 0.749 | 2.523 | 0.448 | 2.250 | 1.672 | 0.4547 |
| 4,500 | 0.750 | 2.292 | 0.500 | 2.147 | 1.500 | 0.5000 |
| 5,000 | 0.747 | 2.105 | 0.555 | 2.060 | 1.346 | 0.5685 |
| 5,920‡ | 0.688 | 1.870 | 0.688 | 1.870 | 1.000 | 1.0000 |

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*Vapor pressure of *n*-hexane.
†Volumes at dew point, calculated.
‡Critical state.

volatility between the components, partial condensation at liquid-nitrogen temperatures was employed. The sample of the gas phase was removed from the heterogeneous mixture under isobaric-isothermal conditions and passed through a special weighing bomb (*13*) which was maintained at liquid-nitrogen temperatures. To ensure that all the *n*-hexane was removed the hydrogen was passed through a second weighing bomb also maintained at liquid-nitrogen temperatures. The total quantity of hydrogen in the sample was determined by volumetric measurement in a large glass vessel maintained at 100°F. The change in pressure within this vessel was determined by means of a mercury-in-glass manometer used in conjunction with a cathetometer. The *n*-hexane and a small quantity of dissolved hydrogen were permitted to warm to room temperature in the weighing bombs and then were recooled to liquid-nitrogen temperatures and the hydrogen was removed by prolonged evacuation. No difficulty was experienced in obtaining measurements reproducible within 0.001 mole fraction *n*-hexane. Measurements upon samples of known compositions yielded results within this error. The techniques developed for partial condensation should have permitted the composition of the gas phase in heterogeneous mixtures of hydrogen and *n*-hexane to be determined within 0.002 mole fraction.

## MATERIALS

The hydrogen, obtained from a commercial manufacturer, was prepared electrolytically and contained 0.005 mole fraction oxygen and, reportedly, less than 0.002 mole fraction of material other than hydrogen and water. The gas was passed through liquid nitrogen, through a chamber containing platinum wire heated to approximately 800°F., and again through a coil immersed in liquid nitrogen. This treatment was followed by contact with activated charcoal and anhydrous calcium sulfate. These processes were carried out at pressures of over 500 lb./sq. in. Mass spectrographic analysis of hydrogen so purified indicated that it contained less than 0.001 mole fraction of material other than hydrogen.

The *n*-hexane was obtained as research grade from the Phillips Petroleum Company, which reported it to contain not more than 0.003 mole fraction of material other than *n*-hexane. The hydrocarbon was dried over metallic sodium and solidified at liquid-nitrogen temperatures. It was maintained at a relatively high vacuum in the solid state for an extended period to complete the removal of noncondensable gases. A value of 40.8707 lb./cu. ft. for the specific weight at 77°F. was obtained for the air-free sample of liquid as compared with 40.878 lb./cu. ft. reported by Rossini (*12*) for an air-saturated sample at the same temperature. The index of refraction relative to the *D* lines of sodium at 77°F. was 1.37225, as compared with 1.37226 reported by Rossini (*12*) for air-saturated *n*-hexane. It is

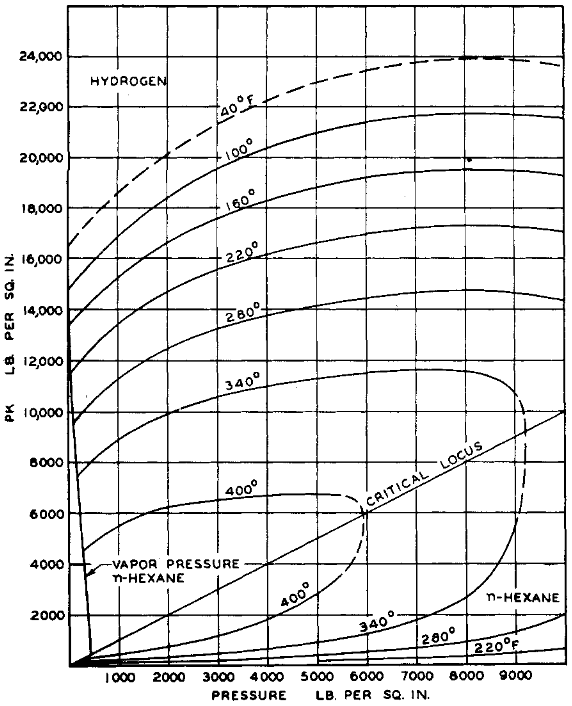

Fig. 3. Equilibrium ratios for hydrogen and *n*-hexane.

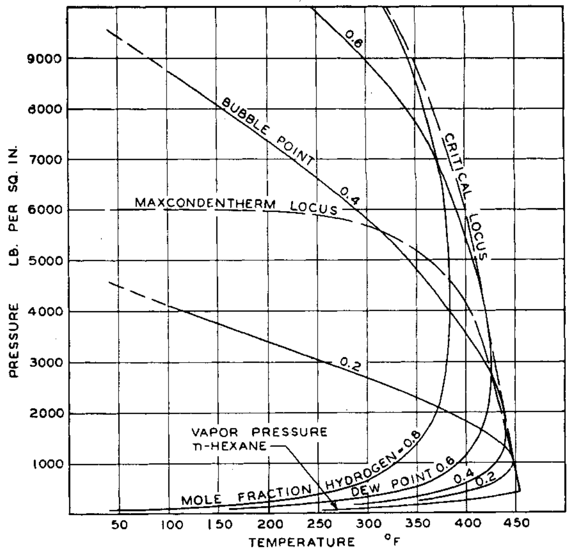

Fig. 5. Pressure-temperature diagram for hydrogen–*n*-hexane system.

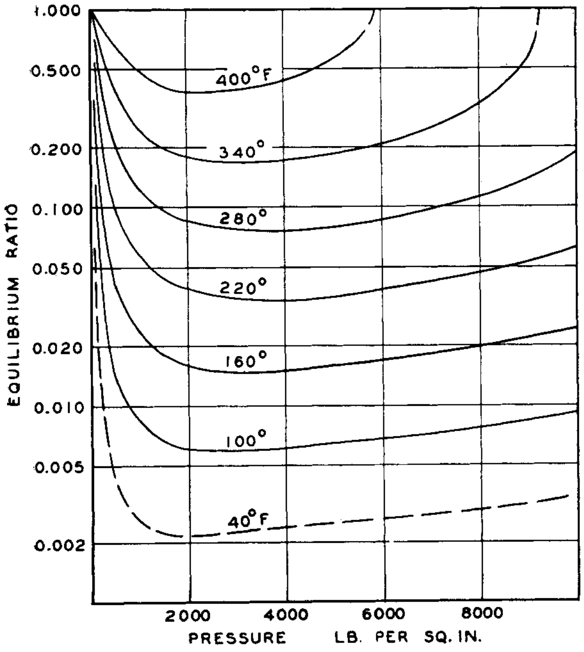

Fig. 4. Equilibrium ratio for *n*-hexane.

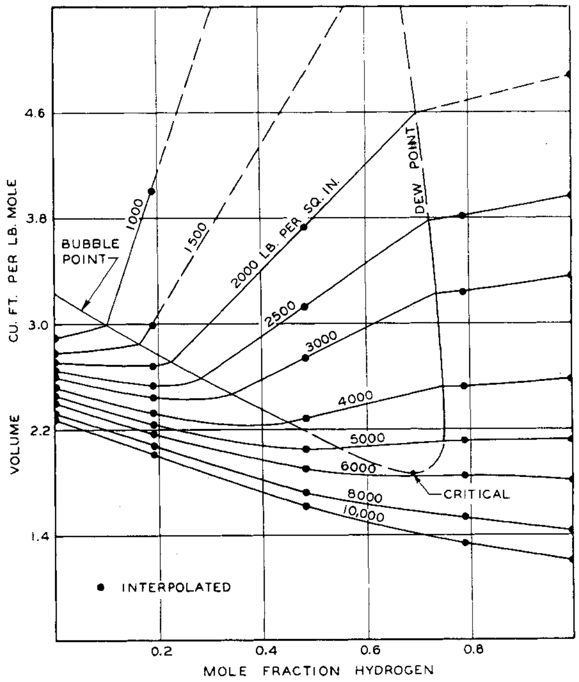

Fig. 6. Molal volume as a function of composition at 400°F.

probable that the material used in this investigation contained less than 0.001 mole fraction of impurities.

## EXPERIMENTAL RESULTS

Measurements of the volumetric behavior of four mixtures of hydrogen and *n*-hexane were investigated. A large sample of each mixture was introduced and measurements were made for pressures from approximately 1,000 to 10,000 lb./sq. in. The sample was then brought to a single-phase state and approximately 80% of it removed. The remaining smaller sample was then investigated over the same temperature interval to obtain data for pressures below 1,000 lb./sq. in. Figure 1 shows the experimental information obtained for a mixture containing 0.1895 mole fraction hydrogen. It is clear that at 100°F. the specific volumes smoothed with respect to composition deviated somewhat from the experimental data for this mixture. Similar experimental information was obtained for each of the three other samples investigated. The detailed record of experimental data obtained in the course of this volumetric study is available (*9*). One mixture containing 0.0298 mole fraction hydrogen did not differ significantly as to volumetric behavior in the liquid phase from pure *n*-hexane and was not used directly in the smoothing of the volumetric data in this region.

The composition of the coexisting phase as determined from condensation analysis of samples withdrawn under isobaric-isothermal conditions from the gas phase of heterogeneous mixtures of hydrogen and *n*-hexane is shown in Figure 2. The scale of the figure in the vicinity of pure *n*-hexane was enlarged markedly in order to illustrate the behavior of the gas phase in somewhat greater detail. The points shown for the liquid phase were obtained from discontinuities in the isothermal first derivative of specific volume as a function of pressure. The data obtained in the course of the measurement of the composition of the gas phase in heterogeneous mixtures of hydrogen and *n*-hexane are also available (*9*).

Figure 3 presents the product of the molal gas-liquid equilibrium ratios and pressure for hydrogen and for *n*-hexane as a function of pressure for each of the several temperatures investigated. The use of the product of pressure and the equilibrium ratio made it possible to present the behavior in greater detail than when the equilibrium ratio alone is employed.

The equilibrium ratio for *n*-hexane is presented in Figure 4 for each of the temperatures investigated. The values for 40°F. are included by extrapolation and indicated by dotted curves. The dew- and bubble-point curves are shown for the four mixtures on a pressure-temperature diagram in Figure 5, the loci of the critical and maxcondentherm states being included. The two-phase pressure exceeds 10,000 lb./sq. in. at temperatures below 320°F.

The variation in volume with composition at 400°F. is presented in Figure 6, which includes the behavior for *n*-hexane (*14*) and hydrogen (*3*). The molal volumes for even values of pressure were interpolated from the experimental data for each mixture. The agreement with the data for *n*-hexane and hydrogen appears satisfactory and was comparable with that shown in Figure 6 for all the temperatures investigated.

Table 1 records the molal volume for even values of pressure and temperature for three experimentally studied compositions. A standard deviation of 0.000036 cu. ft./lb. was found for the experimental data in the liquid phase from the smooth curves from which the tabular information of Table 1 was obtained. The standard deviation of the data in the two-phase region was 0.00044 cu. ft./lb. The much larger deviation in the heterogeneous region probably results from a lack of strict attainment of equilibrium between the phases. The deviation was random, as measurements were obtained upon both increase and decrease in the total volume of the system. The standard deviation cited assumed that all the uncertainty existed in specific volume and that none was associated with the evaluation of pressure, temperature, and composition. The data of Table 1 are smooth with respect to composition within the small uncertainty associated with graphical operations involving volumetric data for *n*-hexane, hydrogen, and the four experimental mixtures investigated.

TABLE 3. ESTIMATED PROPERTIES AT THE UNIQUE STATES IN THE HYDROGEN–*n*-HEXANE SYSTEM*

| Mole fraction hydrogen | Pressure, lb./sq. in. | Temperature, °F. | Pressure, lb./sq. in. | Temperature, °F. |
|---|---|---|---|---|
| | Critical | | Maxcondentherm | |
| 0.0 | 433.9† | 454.6† | 433.9 | 454.6 |
| 0.1 | 690 | 452 | 620 | 452 |
| 0.2 | 1000 | 449 | 840 | 449 |
| 0.3 | 1430 | 445 | 1150 | 446 |
| 0.4 | 2000 | 439 | 1500 | 441 |
| 0.5 | 2790 | 432 | 2010 | 435 |
| 0.6 | 4050 | 419 | 2750 | 425 |
| 0.7 | 6300 | 396 | 3660 | 411 |
| 0.8 | — | 277 | 4590 | 382 |
| 0.9 | — | — | 5450 | 327 |
| 1.0 | 188.1‡ | −399.8‡ | 188.1 | −399.8 |

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*These data are much more uncertain than the directly measured quantities.
†Critical of *n*-hexane.
‡Critical of hydrogen.

Table 2 presents the compositions and molal volumes of the liquid and gas phases of heterogeneous mixtures of hydrogen–*n*-hexane for seven temperatures between 40° and 400°F. In addition, the molal equilibrium ratios for hydrogen and *n*-hexane and estimates of the critical state were included. Table 3 records a number of the properties at the unique states in the heterogeneous region.

## ACKNOWLEDGMENT

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