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Vapor-Liquid Equilibria of Naphthalene-*n*-Dodecane, *n*-Dodecane-Butyl Carbitol, and Naphthalene-Butyl Carbitol Systems at Subatmospheric Pressure

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This investigation is another in a series undertaken to determine vapor-liquid equilibrium characteristics of the heavy hydrocarbon systems under vacuum. Vapor-liquid equilibrium data were determined for the naphthalene-*n*-dodecane, *n*-dodecane-butyl carbitol, and naphthalene-*n*-butyl carbitol systems at a pressure of 100 mm. of mercury absolute, using a modified Colburn still.

MATERIALS

The naphthalene used was c.p. grade material, of the same quality as that used by Ward (14) and Martin (9).

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Experimental values of physical properties of the naphthalene are compared with literature values in Table I. The vapor pressure data for the naphthalene reported in Table I were determined as a function of temperature by boiling the material under fixed subatmospheric pressures in the Colburn still.

The *n*-dodecane was obtained in a relatively pure state and was further purified by fractionation at 100 mm. of mercury pressure in a 1-inch, vacuum-jacketed, glass column packed with 1/4-inch glass helices for 5 feet of its length. Only the constant boiling heart cut was used. Refractive index, vapor pressure, and density data for the purified dodecane agreed closely with literature values

Table I. Properties of Naphthalene, *n*-Dodecane, and Butyl Carbitol

	Naphthalene		<i>n</i> -Dodecane		Butyl Carbitol	
	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.
Refractive index	n_D^{25} 1.5826	1.5822 (5)	n_D^{25} 1.4203	1.4195 (2)	n_D^{27} 1.4290	1.4290 (7)
Density	d_4^{20} 0.750	0.751 (7)	d_{20}^{20} 0.952	0.9536 (6)
	Temperature, °C.					
At Vap. Press., Mm. Hg						
50	124.60	124.90 (12)	127.50	127.54 (12)	142.4	141.4 (13)
80	137.90	137.81	139.75	139.90	154.2	153.3
100	144.35	144.31	146.20	146.14	160.7	159.8
150	156.25	156.81	157.50	158.10	173.2	172.3
200	166.40	166.27	167.40	167.14	181.9	181.2

Table II. Calibration Curves for Analysis of Samples

Naphthalene- <i>n</i> -Dodecane Naphthalene Refractive Index		<i>n</i> -Dodecane-Butyl Carbitol <i>n</i> -Dodecane Refractive Index		Naphthalene-Butyl Carbitol Naphthalene Refractive Index	
Mole %	at 100 °C.	Mole %	At 100 °C.	Mole %	At 100 °C.
0.00	1.39219	0.00	1.40543	0.00	1.40526
9.66	1.40187	10.83	1.40317	10.42	1.41393
16.36	1.41011	20.14	1.40121	21.61	1.42827
22.45	1.41881	31.53	1.39917	30.48	1.44757
35.08	1.43791	40.19	1.30801	38.63	1.45738
48.54	1.45700	50.67	1.39611	50.11	1.48214
58.08	1.47497	58.40	1.39497	60.34	1.50039
69.68	1.49997	68.07	1.39382	69.24	1.51886
82.52	1.53072	80.06	1.39322	79.72	1.54014
93.42	1.56345	89.29	1.39261	89.55	1.56160
100.00	1.58260	100.00	1.39219	100.00	1.58260

(Table I). As a further check of the purity of the compound, a sample was distilled in the Colburn still; the liquid and equilibrium vapor were found to have the same value of refractive index as the original solution. The butyl carbitol was purified by fractionation under vacuum to obtain a constant boiling heart cut. The refractive index of the purified material was 1.4290 at 27 °C., which was the same value reported elsewhere (7). Vapor pressure data were obtained by boiling a sample in the Colburn still. Experimental values of vapor pressure, refractive index, and density are shown in Table I with reported values.

APPARATUS

The modified Colburn still was the same as that used by Martin (9).

The temperature in the residue chamber was measured by a calibrated copper-constantan thermocouple connected to a Leeds & Northrup potentiometer capable of measuring voltage within 1 μ v. (0.03 °C.). Pressures were read from an absolute mercury manometer capable of measuring within 0.05 mm.

A Bausch & Lomb precision refractometer, maintained at 100 ° \pm 0.1 °C., was used to determine the index of refraction of the vapor and liquid samples.

PROCEDURE

The procedure for determination of vapor-liquid equilib-

rium was essentially that described by Haynes (3). In starting a determination of vapor-liquid equilibrium, the vacuum pump was turned on and the pressure in the system was lowered to 100 mm. of mercury. Then the manostat was closed and the pressure regulated to the exact desired value. To prevent solidification of the naphthalene, wet steam was circulated through the condensers, and heat was applied to the residue chamber and stopcock, the vapor chamber, and the vapor condensate chamber and stopcock. The three-way stopcock controlling flow from the condensate chamber to the vaporizer tube was closed. The sample, which had been heated above its melting point in an oven, was introduced into the residue chamber by drawing it up through the liquid sampling stopcock. Approximately 40 cc. of the sample was used in each determination.

The sample was rapidly heated to boiling in the residue chamber, and the vapor condensed in the condensers and collected in the condensate chamber. When the level was high enough in the condensate chamber to cause flow through the vaporizer tube, heat was applied to the tube and the three-way stopcock was opened slightly. The stopcock was adjusted to allow a steady trickle of liquid through the vaporizer tube, and the heat to the vaporizer tube was controlled so that one drop of liquid remained in the dip at the lower end of the tube. This assured that the vapor entering the residue chamber would be saturated.

After constant temperature was reached, approximately

Table III. Vapor-Liquid Equilibrium Data for Naphthalene-*n*-Dodecane System

Temperature, °C.		Naphthalene, Mole %				Naphthalene		<i>n</i> -Dodecane	
Exptl.	Smoothed	x_{exptl}	x_{smoothed}	y_{exptl}	y_{smoothed}	y_{exptl}	γ_{TC}	y_{exptl}	γ_{TC}
144.5	144.5	8.6	8.6	12.8	12.80	1.473	1.485	1.010	1.001
143.2	143.35	16.4	16.4	22.4	22.52	1.416	1.435	1.030	1.005
142.6	142.55	23.3	23.3	30.4	30.30	1.376	1.395	1.031	1.015
142.0	141.9	31.6	31.6	39.0	38.81	1.335	1.320	1.038	1.035
141.2	141.1	42.9	42.9	49.0	48.80	1.275	1.270	1.069	1.065
140.5	140.5	55.0	55.0	57.5	57.51	1.195	1.190	1.162	1.130
140.2	140.2	67.2	67.2	67.15	67.02	1.150	1.114	1.243	1.250
141.0	140.87	81.6	81.6	77.8	76.81	1.057	1.050	1.468	1.525
142.1	142.3	93.0	93.0	92.5	90.05	1.030	1.008	1.915	1.980

Table IV. Vapor-Liquid Equilibrium Data for *n*-Dodecane-Butyl Carbitol System

Temperature, °C.		<i>n</i> -Dodecane, Mole %				<i>n</i> -Dodecane		Butyl Carbitol	
Exptl.	Smoothed	x_{exptl}	x_{smoothed}	y_{exptl}	y_{smoothed}	y_{exptl}	γ_{TC}	y_{exptl}	γ_{TC}
155.5	155.5	4.6	4.6	31.0	30.55	4.880	4.825	0.845	1.007
150.4	150.0	12.5	12.5	44.5	44.00	3.200	3.360	0.885	1.035
145.2	145.2	38.0	28.0	54.0	54.20	1.995	2.060	1.100	1.170
143.2	143.2	46.0	46.0	59.0	59.00	1.425	1.420	1.418	1.450
142.8	142.7	58.5	58.5	62.5	72.50	1.205	1.210	1.718	0.1705
142.5	142.5	74.3	74.3	71.0	70.60	1.089	1.065	2.170	2.200
143.5	143.6	89.5	89.5	83.2	83.50	1.021	1.010	2.955	2.910

Table V. Vapor-Liquid Equilibrium Data for Naphthalene-Butyl Carbitol System

Temperature, °C.		Naphthalene, Mole %				Naphthalene		Butyl Carbitol	
Exptl.	Smoothed	x_{exptl}	x_{smoothed}	y_{exptl}	y_{smoothed}	γ_{exptl}	γ_{TC}	γ_{exptl}	γ_{TC}
158.7	158.85	6.55	6.55	15.24	15.2	1.455	1.459	0.980	1.002
157.1	157.3	12.3	12.3	25.55	25.6	1.370	1.386	0.975	1.007
155.4	155.6	18.3	18.3	34.9	34.8	1.320	1.328	0.973	1.015
153.6	153.5	25.6	25.6	43.9	44.4	1.262	1.260	0.982	1.030
151.0	151.3	36.4	36.4	55.2	55.0	1.195	1.183	1.028	1.058
147.2	147.3	58.8	58.8	72.9	72.8	1.112	1.073	1.132	1.153
145.9	145.9	72.1	72.1	81.2	81.2	1.050	1.035	1.213	1.240
144.8	144.8	87.7	87.7	91.5	91.5	1.015	1.008	1.340	1.368
144.5	144.5	92.7	92.7	94.5	94.6	1.004	1.002	1.404	1.420

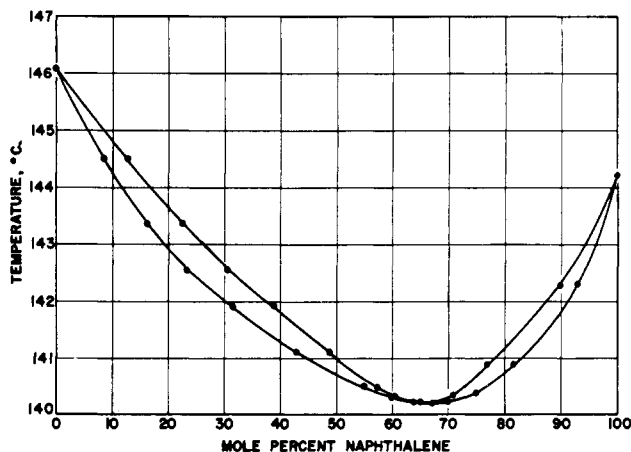


Figure 1. Equilibrium boiling point diagram for *n*-dodecane-naphthalene system at 100 mm. of mercury pressure

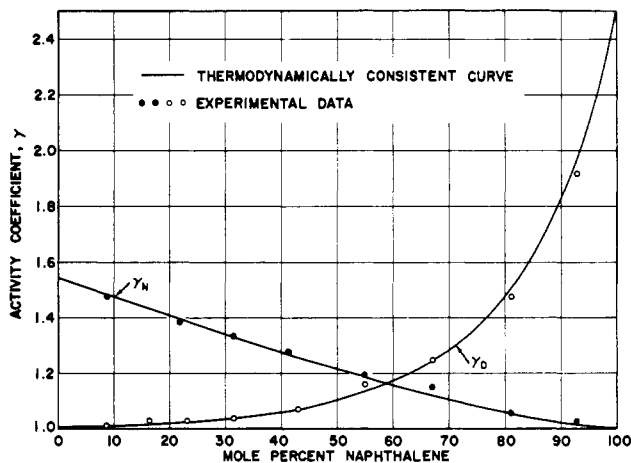


Figure 2. Activity coefficients for *n*-dodecane-naphthalene system at 100 mm. of mercury pressure

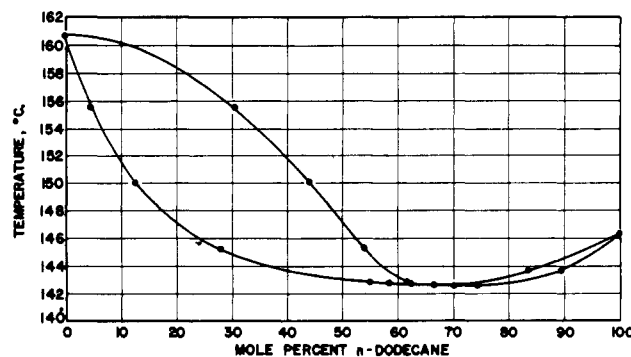


Figure 3. Equilibrium boiling point diagram for *n*-dodecane-butyl carbitol system at 100 mm. of mercury pressure

1 hour was allowed for the sample to reach equilibrium. At that time, the three-way stopcock was closed to prevent mixing of the vapor and liquid samples, the heat to the still was turned off, and the system was allowed to reach atmospheric pressure. Portions of the liquid and vapor samples were first drawn off to flush out the stopcock tips and ensure against contamination. The samples were then drawn into sample bottles and retained for analysis. Compositions of the samples were determined by comparing their refractive index with calibration curves of the refractive index of samples of known composition (Table II). These refractive index data are relative values only, and should not be accepted as absolute values. Little is known about the change in refractive index of the glass refractometer prism with changing temperature, and it is probable that these refractive index data could be reproduced only by duplicating the conditions of this experiment.

CORRELATION OF DATA

In general, at subatmospheric pressures deviations from ideal solution behavior in the liquid phase are of greater magnitude than deviations from ideal behavior of the vapor phase. The thermodynamic relation, Equation 1, is commonly used to describe equilibrium between vapor and liquid phases at constant temperature and pressure.

$$x_1 \left(\frac{\partial \ln f_1}{\partial x_1} \right)_{\pi, T} + x_2 \left(\frac{\partial \ln f_2}{\partial x_1} \right)_{\pi, T} + x_3 \left(\frac{\partial \ln f_3}{\partial x_1} \right)_{\pi, T} + \dots = 0 \quad (1)$$

For a binary mixture, $dx_1 = -dx_2$, and

$$x_1 \left(\frac{\partial \ln f_1}{\partial x_1} \right)_{\pi, T} = x_2 \left(\frac{\partial \ln f_2}{\partial x_2} \right)_{\pi, T} \quad (2)$$

If the conditions allow the vapor to behave as an ideal gas, the equation can be expressed as:

$$x_1 \left(\frac{\partial \ln P_1}{\partial x_1} \right)_{\pi, T} = x_2 \left(\frac{\partial \ln P_2}{\partial x_2} \right)_{\pi, T} \quad (3)$$

Equation 3 (Duhem equation) is applicable to a binary, two-phase system under conditions such that the perfect-gas law applies to the vapor, at constant temperature and at constant pressure. In many cases it applies satisfactorily to a binary two-phase system if they are at constant temperature and a variable total pressure equal to the vapor pressure. The deviations in the liquid phase are expressed in terms of γ , activity coefficient. The activity coefficient data given in Tables III, IV, and V were calculated from the following relation.

$$\gamma = \frac{\nu y \pi}{x P} \quad (4)$$

The values of the fugacity coefficient, ν , were determined using the generalized charts of Hougen and Watson (4). Values of critical temperatures and critical pressures for

naphthalene and *n*-dodecane were taken from the literature (2), and values for butyl carbitol were estimated by Lydersen's method (8). From the Hougen and Watson charts, by using the test pressure and temperatures, the fugacity coefficients for each of the three compounds were found to be essentially equal to unity.

The "thermodynamically consistent" data shown in Tables III, IV, and V were calculated from the van Laar equations as modified by Carlson and Colburn (1).

$$\log \gamma_1 = \frac{Ax_2^2}{[x_1A/B + x_2]^2} \quad (5)$$

$$\log \gamma_2 = \frac{Bx_1^2}{[x_1 + x_2B/A]^2} \quad (6)$$

A is the terminal value of $\log \gamma_1$, where $x_1 = 0$, and *B* is the terminal value of $\log \gamma_2$, where $x_2 = 0$. Using Equations 5 and 6, determination of γ_1 and γ_2 at a single known composition permits evaluation of *A* and *B* and calculation of the complete activity coefficient curves. This was the procedure used in calculating the data plotted in Figures 2, 4, and 6, and listed as "thermodynamically consistent" data in Tables III, IV, and V. Applying a "standard deviation" relation (Equation 7) to the differences between the experimental activity coefficients and those derived from the van Laar relations and using the average values of *A* and *B*, the average deviations in activity coefficients are as follows:

<i>n</i> -Dod.-Naph.		<i>n</i> -Dod.-Bu. Carb.		Naph.-Bu. Carb.	
<i>n</i> -Dod.	Naph.	<i>n</i> -Dod.	Bu. carb.	Naph.	Bu. carb.
0.021	0.010	0.076	0.090	0.012	0.014

$$\omega = \left[\frac{\sum x^2 - (\sum x)^2/n}{n-1} \right]^{1/2} \quad (7)$$

where x = deviation of experimental activity coefficient values from calculated values
n = number of experimental points
 ω = average deviation

The probable average experimental error in the data is estimated to be in the neighborhood of 1%. Where the data could not be correlated by the van Laar equation, an effort was made to correlate by means of the Margules equations (11), as follows:

$$\ln \gamma_1 = bx_2^2 + cx_2^3 \quad (8)$$

$$\ln \gamma_2 = bx_1^2 + cx_1^3(0.5 + x_2) \quad (9)$$

If $(\ln \gamma_1)/x_2^2$ is plotted vs. x_2 , and $(\ln \gamma_2)/x_1^2$ is plotted vs. $(0.5 + x_2)$, they will both give a line of slope *c* and intercept *b*. Only one experimental point is needed to evaluate both *c* and *b*.

Redlich and Kister (10) outline a method of determining whether or not a binary system is thermodynamically consistent. They developed the following relation:

$$\int_0^x \log \frac{\gamma_1}{\gamma_2} dx_1 = 0 \quad (10)$$

If $\log \gamma_1/\gamma_2$ is plotted as ordinate against x_1 as abscissa, the areas beneath the curve below and above the zero ordinate value are equal if the system is thermodynamically consistent.

The smoothed data on temperature vs. composition shown in Tables III, IV, and V, and in Figures 1, 3, and 5 were obtained by visual smoothing of the curves drawn from experimental liquid composition and activity coefficient data to calculate the smoothed value of vapor composition, using Equation 4.

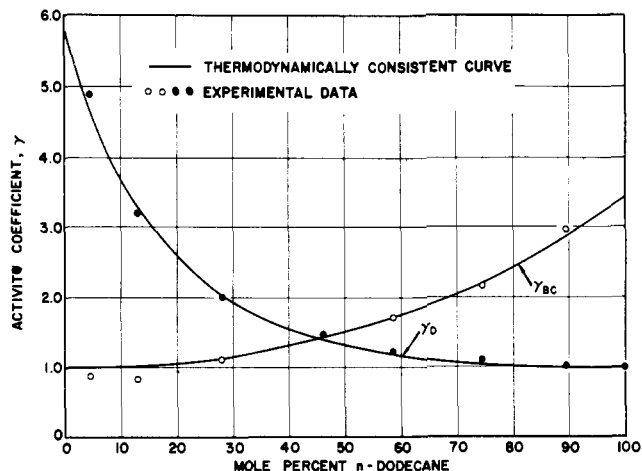


Figure 4. Activity coefficients for *n*-dodecane-butyl carbitol system at 100 mm. of mercury pressure

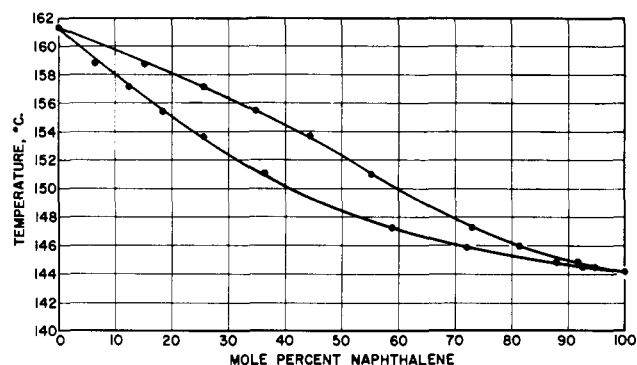


Figure 5. Equilibrium boiling point diagram for naphthalene-butyl carbitol system at 100 mm. of mercury pressure

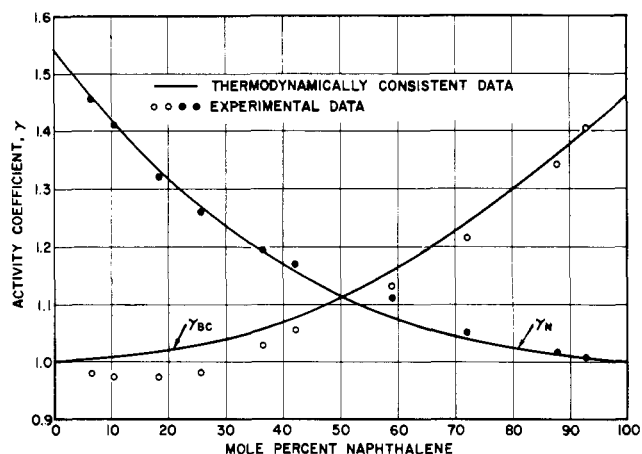


Figure 6. Activity coefficients for naphthalene-butyl carbitol system at 100 mm. of mercury pressure

RESULTS AND CONCLUSIONS

Vapor-liquid equilibrium data were obtained for the naphthalene-*n*-dodecane, *n*-dodecane-butyl carbitol, and naphthalene-butyl carbitol systems at a pressure of 100 mm. of mercury absolute. These data are presented in Tables III, IV, and V and in Figures 1 through 6.

Figure 2 shows good agreement between experimental and thermodynamically consistent values of γ for the naphthalene-*n*-dodecane system. For the *n*-dodecane-butyl carbitol system, some experimental values of activity coefficient below 1.0 are shown for butyl carbitol in the

low dodecane concentration region. However, the remainder of the experimental γ values for butyl carbitol and all values for *n*-dodecane agree very well with the van Laar equation results, as shown in Figure 4. For the naphthalene-butyl carbitol system, values of γ above and below 1.0 were found for butyl carbitol (Figure 6), and it was impossible to correlate this system with the van Laar equation. An unsuccessful effort was made to correlate this system by means of the Margules equation.

Figure 1 shows an azeotrope at approximately 67% naphthalene and 140.2°C. for the naphthalene-*n*-dodecane system. Figure 3 shows an azeotrope at approximately 65% *n*-dodecane and 142.6°C. for the *n*-dodecane-butyl carbitol system.

Figure 5 indicates that the naphthalene-butyl carbitol system exhibits a slight tendency toward azeotrope formation at high naphthalene concentrations. As in the *n*-dodecane-butyl carbitol system, this binary shows unusual behavior, in that activity coefficients above and below 1.0 are found for butyl carbitol. This system could not be correlated using the van Laar equations. This peculiar behavior has been noted before (3, 9, 14). It can possibly be explained through molecular association at low concentrations of the higher aromatic in the binary.

NOMENCLATURE

- A* = constant of van Laar solution of Gibbs-Duhem equation
B = constant of van Laar solution of Gibbs-Duhem equation
b = constant of Margules solution of Gibbs-Duhem equation
c = constant of Margules solution of Gibbs-Duhem equation
 d_{20}^{20} = density at 20°C.
f = fugacity
 f^i = fugacity of pure component at total pressure
 n_D^t = index of refraction at temperature *t*, using sodium *D* light
*P*₁ = vapor pressure of component 1 at temperature of solution, mm. Hg
*x*₁ = mole fraction of component 1 in liquid phase

- x*₂ = mole fraction of component 2 in liquid phase
y = mole fraction of component in vapor phase
 π = total pressure of system, mm. Hg absolute
 ν = fugacity coefficient
 γ = activity coefficient

Subscripts

- BC = butyl carbitol
 D = *n*-dodecane
 exptl = experimental
 N = naphthalene
 TC = thermodynamically consistent

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Some Volatility Characteristics of Aircraft Jet Fuels

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To aid in the design of a combustion system for jet engines, certain information regarding the volatility of the various potential fuels is required. Use of the fuel as a heat sink in supersonic aircraft introduces considerable preheat before injection into the combustion chamber. The preheat and/or the pressure drop across the nozzle cause a certain portion of the fuel to vaporize. The final ratio of vapor to liquid depends on many factors, including the initial pressure, initial temperature, final pressure, and heat losses or influx from or to the fuel.

Considerable vapor-liquid equilibrium data have been recorded for binary and ternary hydrocarbon systems (2), but relatively little work has been done on multicomponent systems. Work in this field has been limited to mixtures of

known composition plus some scattered data obtained by various petroleum companies on their own refinery streams (3). Several methods of calculating flash equilibrium data from ASTM distillation data have been proposed (3, 4, 7). None of these is too satisfactory, as the deviations from the mean range from 12° to 40° F. at atmospheric pressure and are still higher at elevated pressures. The present work was undertaken in order to obtain flash equilibrium data on commercial jet fuels at pressures and temperatures characteristic of those to be expected in engine operation.

The flash equilibrium data were obtained in a laboratory flash equilibrium still. The still design was adapted from that successfully used by several other investigators to obtain flash equilibrium data (6, 8). Standardization runs