

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

Table I. Physical Properties of Test Fuels

	Sample A, JP-4	Sample B, JP-4	Sample C, JP-4	Sample D, JP-5
Gravity, °API	49.4	55.9	48.2	42.7
Distillation, ASTM D-86, % recovered				
IBP	123	152	124	274
5	202	200	214	325
10	240	217	251	347
20	285	236	277	368
30	302	252	290	382
40	327	266	300	404
50	347	278	314	420
60	367	292	340	434
70	390	304	367	451
80	419	319	405	470
90	449	334	450	496
95	470	348	484	515
EP	486	378	514	542
% recovered	98.5	98.0	98.8	98.0
% residue	1.0	1.0	0.9	1.2
% loss	0.5	1.0	0.3	0.8

were made by charging a toluene-iso-octane blend to the still and comparing the results with published data for this system (5).

In this equilibrium study, data were recorded under isothermal conditions; and isenthalpic data were calculated by heat and material balances. These data represent the two thermal extremes. The engine designer can then provide for the most severe conditions and estimate for any intermediate thermal condition.

A family of equilibrium curves for pressures from 5 pounds per square inch absolute to 20 atm. was obtained for each of the three fuels meeting JP-4 specifications and one fuel meeting JP-5 specifications. These fuels represent the extremes of volatility of commercial production of JP-4 and a typical JP-5. A typical JP-4 (sample A) was used to develop the detailed procedure. A manufacturer of

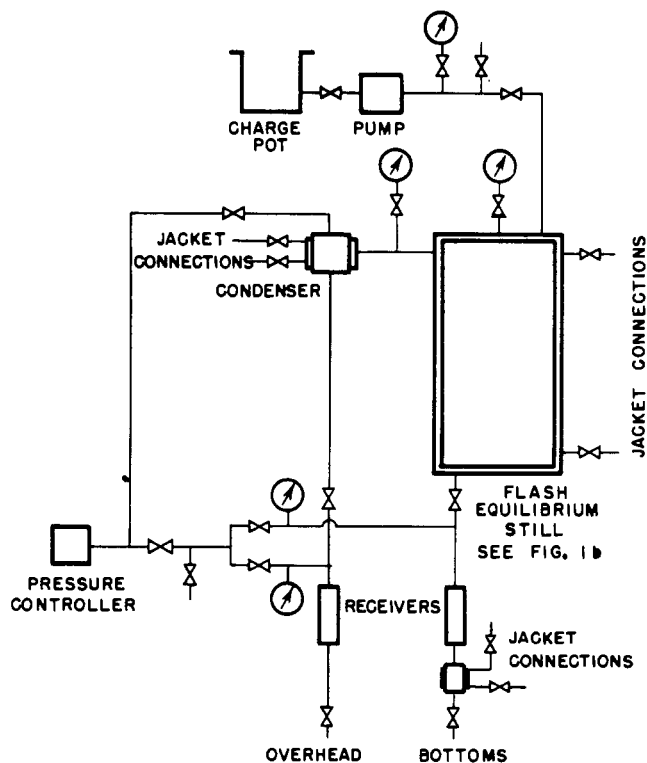


Figure 1. Schematic diagram of flash equilibrium still

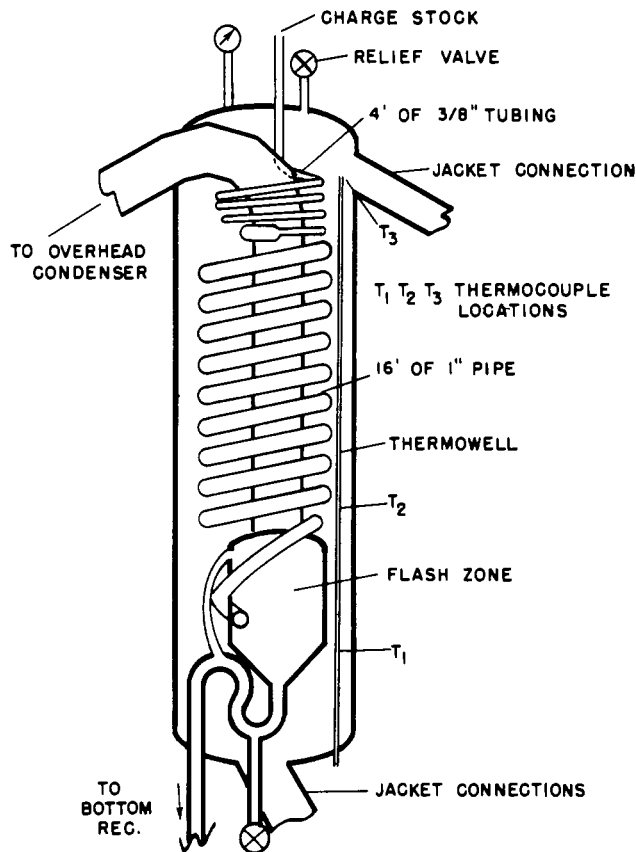


Figure 2. Flash equilibrium still

aircraft jet engines made available for extension of this work the following samples:

1. A JP-4 representing the most volatile commercial product (sample B).
2. A JP-4 intended to represent the least volatile commercial product (sample C). Actually this sample was slightly more volatile than sample A.

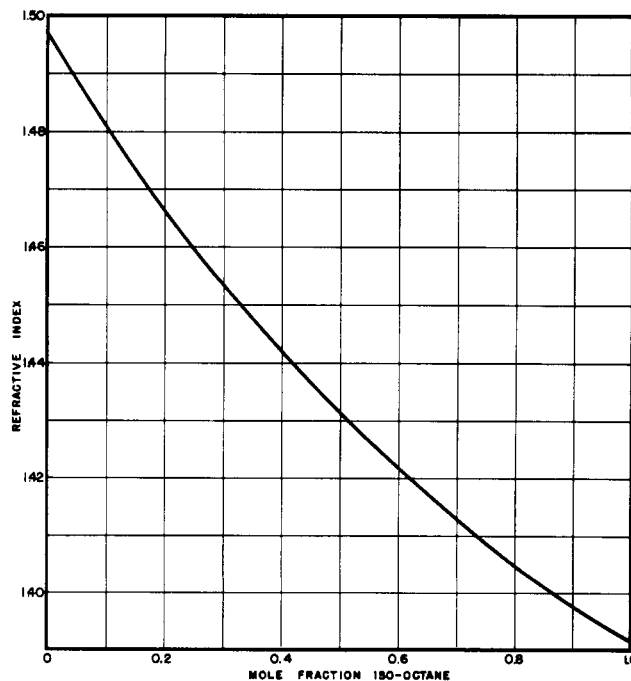


Figure 3. Equilibrium data for toluene-iso-octane
Mole fraction iso-octane vs. refractive index

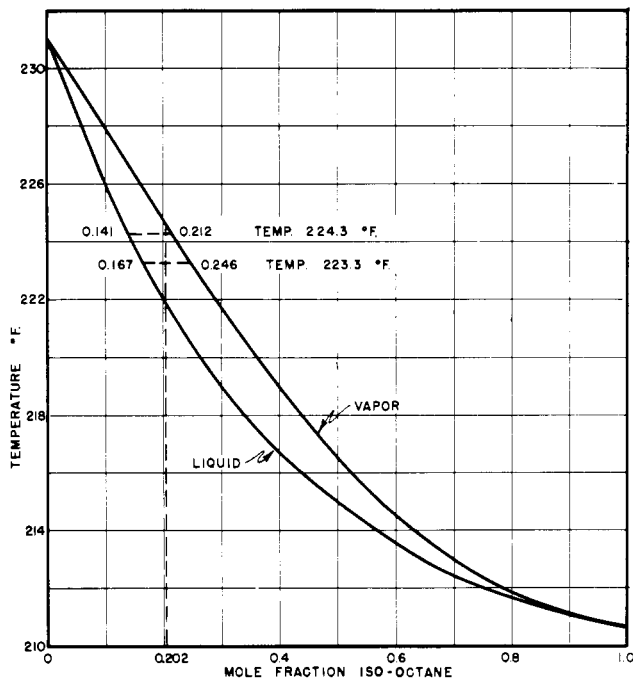


Figure 4. Equilibrium data for toluene-iso-octane
Mole fraction iso-octane vs. boiling point

3. A typical commercial JP-5. Only one sample was needed to define the JP-5 volatility range, as there are only five suppliers of this product; and the spread of distillation range among these five is only 25° to 30° F. One sample in the middle of this distillation spread was obtained (sample D).

Table 1 gives the physical properties of the four fuels studied.

EQUIPMENT

The equipment consisted of a continuous flash equilibrium still shown in Figures 1 and 2. The still was designed to allow a maximum opportunity for equilibrium to be attained. Charge stock was pumped at a constant rate of 1 liter per hour through an extended preheating section

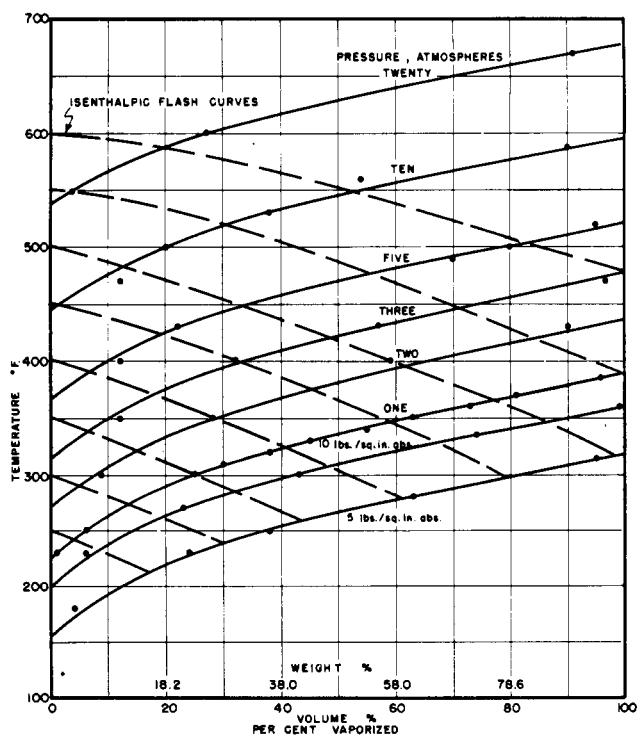


Figure 5. Flash equilibrium and isenthalpic curves for sample A

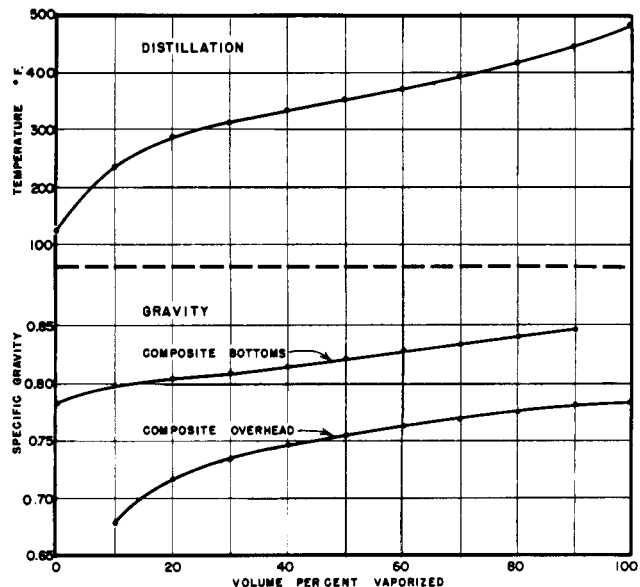


Figure 6. ASTM D-86 distillation and gravity for sample A

which consisted of 4 feet of 3/8-inch 18-gage tubing. In order to provide room for expansion and reduce the pressure drop as the fuel began to vaporize, it was expanded into a 16-foot length of 1-inch schedule 40 pipe. The equilibrium mixture of liquid and vapor tangentially entered the flash zone which was composed of 6 inches of 6-inch schedule 40 pipe. The vapors were withdrawn overhead through a 2-foot length of 3-inch pipe, and the liquid was withdrawn at the bottom. The entire still system exposed to the jet fuel stream was constructed of Type 304 stainless steel.

The preheater and the flash zone were all enclosed in a heating jacket made of 12-inch pipe. The heating medium was circulated as a vapor through the jacket by means of an external boiler, thus always employing a condensing vapor to heat the still. Steam was used for temperatures up to 365° F. and suitable Dowtherms were used for higher temperatures.

Temperatures were measured in the jacket by three thermocouples placed at different heights as shown in Figures 1 and 2. A Milton Roy MiniPump was used to meter

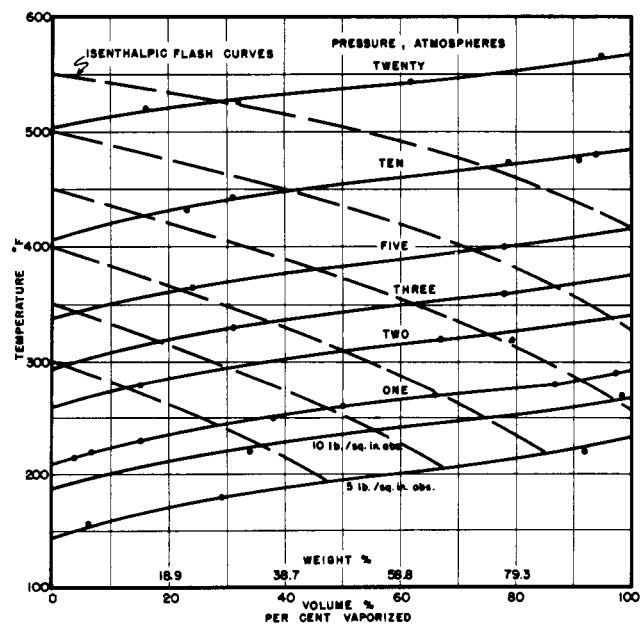


Figure 7. Flash equilibrium and isenthalpic curves for sample B

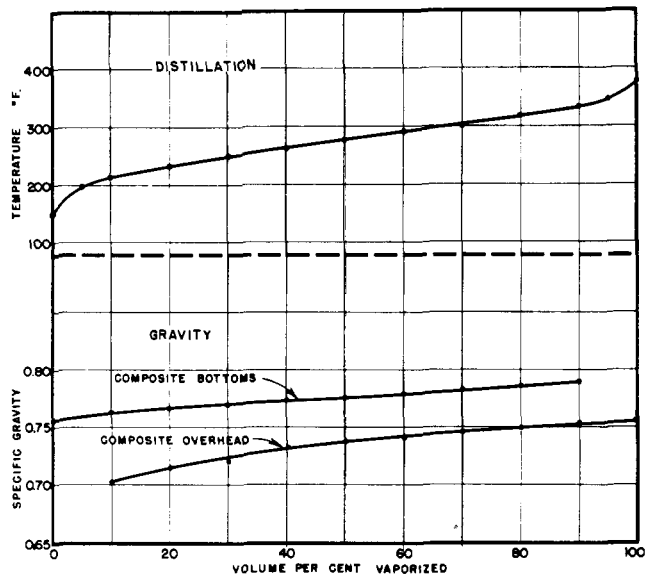


Figure 8. ASTM D-86 distillation and gravity for sample B

the charge stock. Nitrogen was used to provide the back pressure for superatmospheric operation.

EXPERIMENTAL

Each run was made at constant temperature and pressure. Temperatures were read to 1° F., and the maximum spread among the three indicated temperatures was held to 1° F. These temperatures were not permitted to vary more than ±1° F. during a run. Variations in pressure were held to ±0.5 inch of mercury for subatmospheric runs, ±1 pound per square inch for pressures from 1 to 5 atm., and ±5 pounds per square inch for pressures from 10 to 20 atm.

Volume per cent overhead was measured by collecting 10-minute samples of overhead and bottoms until three successive samples yielded results with a maximum spread of 1%. The average of these three readings was recorded as the per cent vaporized.

The length of time required for steady-state conditions to

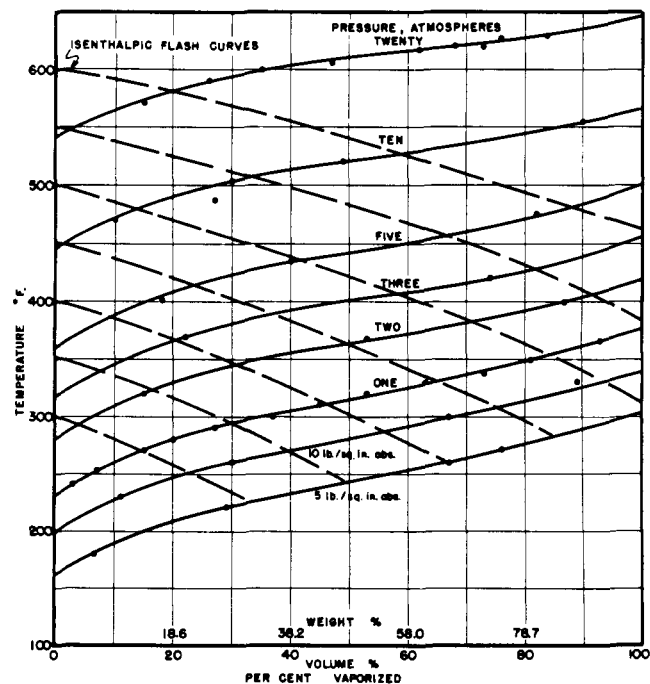


Figure 9. Flash equilibrium and isenthalpic curves for sample C

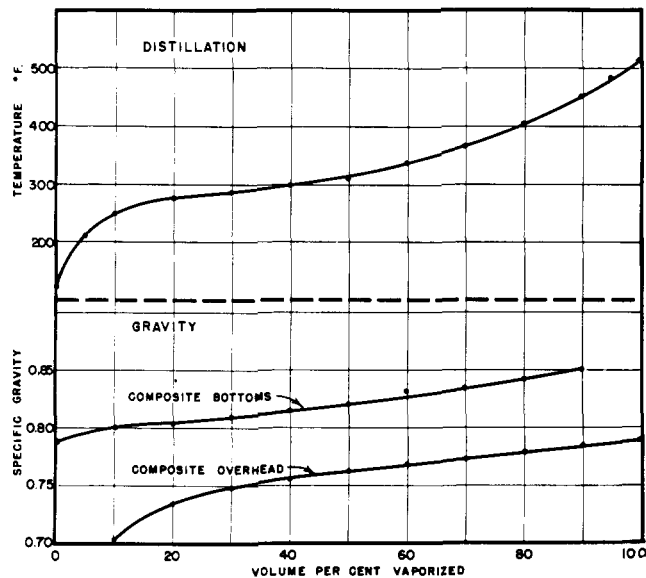


Figure 10. ASTM D-86 distillation and gravity for sample C

be attained varied from 30 to 60 minutes after the temperature and pressure became constant. The existence of steady-state conditions was determined by the method of collecting successive samples as described above.

STANDARDIZATION

In order to determine whether equilibrium conditions could be produced in the still, two standardization runs were made at carefully controlled conditions. All three jacket temperatures were identical, and no detectable variation in any of the temperatures was permitted during the course of the run. The data obtained were checked against those available from the literature (5). The toluene-iso-octane system was chosen because the components and the literature data were readily available. Nitration grade toluene and ASTM reference fuel grade iso-octane, both over 99% pure, were used.

The literature data were plotted as refractive index and temperature vs. the mole fraction of iso-octane (Figures 3 and 4). As these data were reported at a pressure of 760 mm. and the standardization work was done at the prevailing barometric pressure (733 mm.), the recorded still temperatures were corrected by the following equations (1):

$$\text{Iso-octane. } \log p = 6.81189 - \frac{1257.840}{t + 220.735}$$

$$\text{Toluene. } \log p = 6.95464 - \frac{1344.800}{t + 219.482}$$

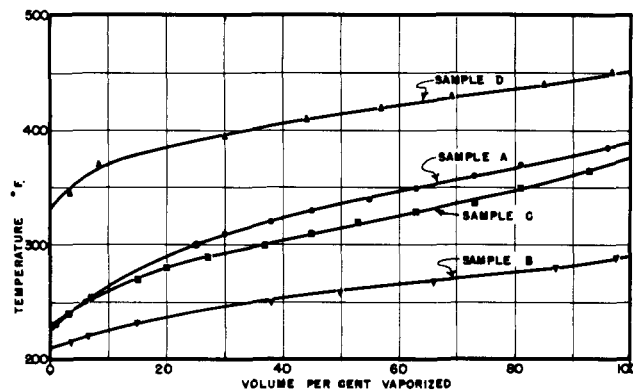


Figure 11. Flash equilibrium curves at atmospheric pressure Various jet fuels

where p is the absolute pressure in millimeters of mercury and t is the boiling point in degrees centigrade.

The temperature corrections were calculated as 1.273°C . for iso-octane and 1.268°C . for toluene. As the difference between these corrections was less than the experimental error, an average value of 1.270°C . (2.3°F .) was used.

During the still run samples of charge, overhead, and bottoms were obtained. The refractive indices were measured; and from Figure 3, the concentrations of iso-octane in each stream were determined. The measured still temperatures were corrected by adding 2.3°F ., and from Figure 4 the concentrations of iso-octane that should be in the overhead and bottoms were determined. The results obtained by analyzing the streams and the expected results obtained from Figure 4 are compared in Table II.

The comparison of the data indicates that under the operating conditions used, equilibrium was closely approximated in the still, and that close approximations to true temperatures were measured, although the thermocouples were in the jacket rather than in the still.

RESULTS

After the standardization work was completed, data were obtained for several JP-4 jet fuels. A family of flash vaporization curves was obtained under isothermal conditions for sample A at pressures ranging from 5 pounds per square inch absolute to 20 atm. Curves were obtained at pressures of 5 and 10 pounds per square inch absolute and at 1, 2, 3, 5, 10, and 20 atm. The curve at atmospheric pressure was carefully defined by obtaining a large number of points along its length. As the curves belong to a family, only four or five points were needed to define the curves at other pressures.

Complementary isenthalpic curves were calculated by heat and material balances for the temperature and pressure ranges. The families of flash vaporization and isenthalpic curves are shown in Figure 5. As the original data were reported in volume per cent and the calculations were on a weight basis, data from an Engler type distillation (Figure 6) were used to calculate the weight per cent comparable with volume per cent.

The other two samples of JP-4 jet fuel (samples B and C) were similarly investigated throughout the temperature and pressure ranges. The curves for these samples are shown in Figures 7 to 10. These three jet fuels effectively covered the range of volatilities normally found in commercial JP-4's. Figure 11, which shows the flash equilibrium data at atmospheric pressure for all the fuels, illustrates the range of volatilities investigated.

Points on the isenthalpic curves were calculated by the following procedure.

Table II. Experimental Standardization Data for Toluene-Iso-octane

Base Stocks		R.I.	Mole Fraction Iso-octane, Figure 3			
Toluene		1.4968	—			
Iso-octane		1.3920	—			
Blend		1.4658	0.202			
			Overhead		Bottoms	
Temperature, $^{\circ}\text{F}$.			Mole Fraction Iso-octane		Mole Fraction Iso-octane	
Recorded	Corrected	R.I.	Exptl. ^a	Lit. ^b	R.I.	Exptl. ^a Lit. ^b
221	223.3	1.4611	0.239	0.246	1.4718	0.160 0.167
222	224.3	1.4628	0.227	0.212	1.4740	0.142 0.141

^aFrom Figure 3.

^bFrom Figure 4.

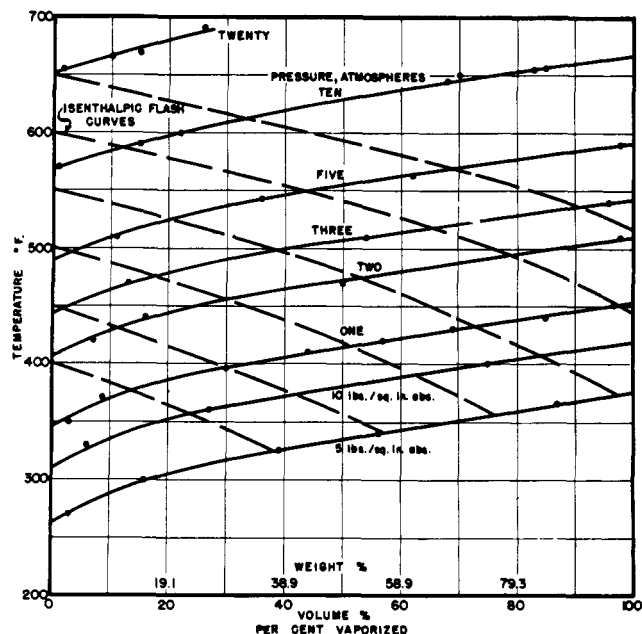


Figure 12. Flash equilibrium and isenthalpic curves for sample D

A temperature representing the bubble point of the liquid is selected. This liquid is then expanded to some lower pressure. At this point, a trial and error calculation is necessary to determine the final temperature. After a final pressure is chosen and a final temperature assumed, the experimental flash vaporization curves are used to obtain the per cent vaporized. When the initial and final conditions are thus established, enthalpy data (7) are used to calculate the enthalpies of the liquid and vapor. If the correct final temperature has been assumed, the two enthalpies (feed and expanded product) will be equal. A difference in these enthalpies requires additional trials until the balance is obtained.

A similar family of curves was obtained for a typical sample of JP-5 jet fuel. These data are given in Figures 12 and 13.

DISCUSSION OF RESULTS

The shapes of the flash curves are similar to the corresponding ASTM distillation curves, although the equilibrium

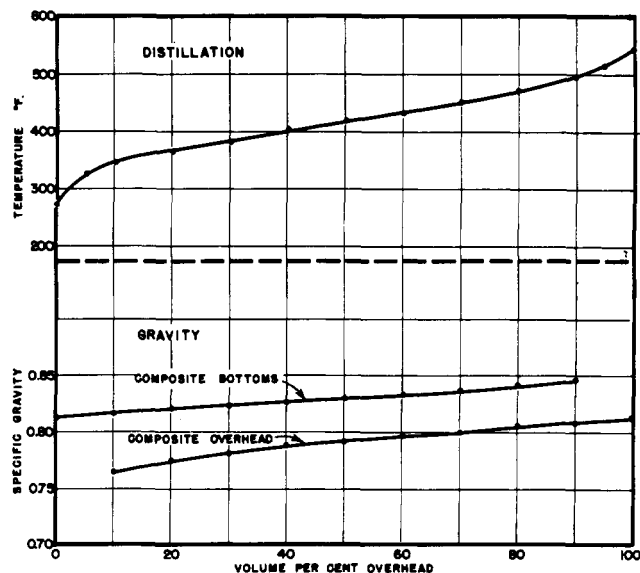


Figure 13. ASTM D-86 distillation and gravity for sample D

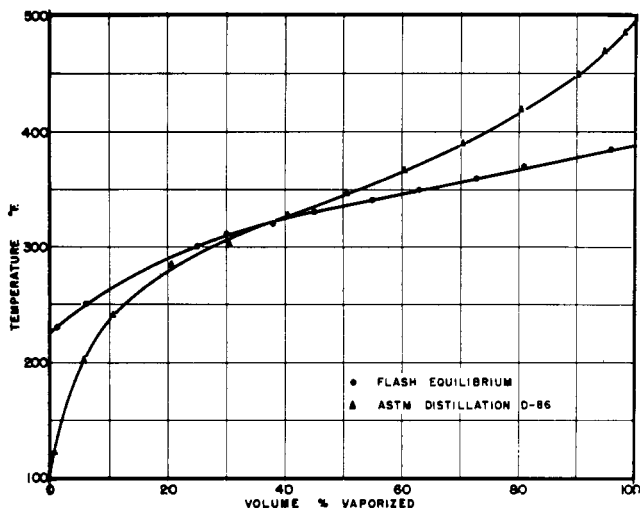


Figure 14. ASTM D-86 distillation and flash equilibrium data at atmospheric pressure for sample A

curve is flatter. Figure 14, showing a plot of both the ASTM D-86 distillation curve and the flash equilibrium curve at atmospheric pressure for sample A, illustrates this point. This is in accord with the expected results for these types of data (3, 4, 7). On the flash curve, the point corresponding to the ASTM initial boiling point is high because of the suppressing effect of the heavy ends. The reduced slope and lower end point are caused by the partial pressure effect of the light ends.

The effect of pressure is, of course, to reduce vaporiza-

tion at a given temperature; however this becomes less pronounced at elevated pressures. For example, in the case of sample A an increase in the pressure from 1 to 3 atm. has approximately the same effect on vaporization as an increase from 10 to 20 atm. Thus, at 390° F. (see Figure 5), increasing the pressure from 1 to 3 atm. decreases the volume per cent overhead from 100 to 28; while at 595° F. increasing the pressure from 10 to 20 atm. results in an almost identical decrease in overhead of 99 to 24.

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Phase Relations of Nitric Acid-Nitrogen Dioxide and Nitric Acid-Water Mixtures at Physicochemical Equilibrium

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The volumetric phase relations of liquid nitric acid at physical and chemical equilibrium have been presented (5). It was shown that the pure acid is unstable at temperatures above its melting point ($-41.59^{\circ}\text{C}.$) and that it develops a high gas pressure when stored in a closed container if the ratio of the vapor space to the total volume of the container is small. As the concentrated nitric acid of commerce contains excess water and nitrogen dioxide, it is of interest in connection with the storage and handling of the acid to know the effect of these additives on its equilibrium pressure.

To obtain the required data, an investigation of the volumetric phase relations of the system nitric acid-nitrogen

dioxide-water is necessary. As a preliminary step to such an investigation, the phase relations of nitric acid-nitrogen dioxide mixtures containing up to 15% by weight of nitrogen dioxide and of nitric acid-water mixtures containing up to 5% by weight of water were determined under conditions of physicochemical equilibrium. The selected concentration range is of particular interest in the field of liquid rocket propellants. The measurements were made between 85° and $150^{\circ}\text{C}.$ and for the ratios of the vapor volume to total volume, (V^g/V), between 0.8 and near the bubble point. The results are summarized here.

Corcoran, Reamer, Duffy, and Sage (1, 2) have investigated the volumetric and phase behavior of the nitric acid-nitrogen dioxide and the nitric acid-water systems, but their

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