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DETERMINATION OF THERMODYNAMIC
PROPERTIES OF AEROZINE-50

Phase I Report

27 December 1966 to 27 January 1967

by

JOSEPH P. COPELAND
JOHN A. SIMMONS
JACK M. SPURLOCK

for

MANNED SPACECRAFT CENTER
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Contract No. NAS9-6720

Atlantic Research Corporation
Alexandria, Virginia
April 21, 1967

ATLANTIC AR RESEARCH

PROPRIETARY DATA

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ALEXANDRIA, VIRGINIA

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1.0 SUMMARY

This report describes the results of the first phase of a program to determine the thermodynamic properties of the propellant, Aerozine-50 (a 1:1 mixture of hydrazine and UDMH[*]), which are to be presented in useful charts and tables showing the corresponding values of enthalpy, entropy, phase composition, pressure, temperature and specific volume.

The first phase of the program has included (1) a survey and evaluation of pertinent data reported in the literature, (2) selection of the most appropriate methods of correlating the data and calculating values of the thermodynamic properties, (3) determination of what data is lacking or unreliable, and must be measured, (4) delineation of the experiments and techniques to accomplish this, and (5) selection of the most appropriate means to present the derived thermodynamic properties. Phase II of this program will consist of the final design and construction of the required experimental apparatus, the performance of the measurements, correlation of the data and preparation of the charts and tables.

The establishment of the thermodynamic properties requires several kinds of data. These include p-V-T data for the components, hydrazine and UDMH, and their mixtures, activity coefficients for the liquid phase, heats of phase transition, composition variations for phase transitions and thermodynamic functions for the components in the ideal gas state. Some of these data have been reported for Aerozine-50 in the literature, but all are not reliable. In particular, the survey and evaluation of reported data, accomplished in Phase I, revealed the following:

(a) Both hydrazine and UDMH undergo thermal decomposition at moderate to high temperatures and react or decompose catalytically when in contact with certain materials, even at low temperatures. These characteristics

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[*]Unsymmetrical dimethylhydrazine

have plagued previous experiments with these liquids and make much of the data reported suspect.

(b)   Pertinent data reported for UDMH include the enthalpy and entropy of the ideal gas, latent heat of vaporization, vapor pressure, and the heat capacity of the solid and liquid. These data appear to be reliable, except the values of vapor pressure determined at higher temperatures or in contact with mercury (manometric fluid).

(c)   Pertinent data reported for hydrazine include the heat capacity of the solid and liquid, vapor pressure, heat of fusion, latent heat of vaporization and the enthalpy and entropy of the ideal gas. All these data appear reliable except for the data for vapor pressure at high temperatures.

(d)   Data reported for mixtures of hydrazine and UDMH include liquid-vapor phase equilibria (p-T-x-y data), density and specific heat of liquid Aerozine-50, and the freezing compositions including an eutectic composition of 94 mole per cent UDMH.

From these results it is apparent that additional data must be measured in order to verify or correct suspect values and to obtain missing values. The types of data needed are the p-V-T properties of mixtures of UDMH and hydrazine vapors, p-T-x-y data for liquid-vapor phase equilibria, the vapor pressure of the freezing and eutectic mixtures, and the densities of liquid Aerozine-50 and hydrazine-rich mixtures. In order to minimize the number of measurements required for this, empirical and analytical correlations have been selected to provide an accurate means of interpolation and extrapolation of data. These include the Redlich-Kwong equation of state (for p-V-T data) and a three constant correlation of solution activity coefficients.

The preliminary design of the apparatus for the needed experiments has been completed. Measurements of p-V-T properties and phase equilibria will be obtained with a well-stirred, constant-volume pressure cell. Provision will be made for drawing samples of the phases present;

the composition of the samples will be determined by gas-chromatography. To avoid the use of reactive manometric fluids, pressure will be measured by a precision, diaphragm-type transducer. A constant temperature bath, sample traps, a charging vessel and vacuum system will comprise the accessory equipment.

Since many materials either react with hydrazine and UDMH or catalyze their decomposition, the inertness of candidate materials for the experimental apparatus must be proved experimentally. For this purpose the materials will be immersed in the liquid and vapor of UDMH-hydrazine mixtures for several hours at selected temperatures. Reaction or decomposition will be detected by chemical analysis of the liquid and comparison of vapor pressure measurements at a given temperature.

Pure samples of UDMH and hydrazine for the experiments will be obtained by fractional distillation, at room temperature and reduced pressure, of the commercially available materials.

2.0   INTRODUCTION

The thermodynamic properties of Aerozine-50 (a 1:1 mixture of hydrazine and UDMH*) are of major importance to research, development and design efforts concerning the use of Aerozine-50 as a propellant or hydraulic working-fluid in space propulsion systems. Recent studies[2] have shown that upon exposure to a low-pressure environment, Aerozine-50 can undergo rapid evaporative cooling, and both composition and phase changes, including freezing. When used as a fuel in a rocket engine these phenomena can, in turn, produce severe and even extremely dangerous igni-tion irregularities, such as delayed and explosive ignition. Other studies[24] have demonstrated that Aerozine-50,when used as a hydraulic fluid for the actuation of propellant valves, can freeze upon leaking or intentional venting into a vacuum and thereby often cause severe malfunc-tions of the valve. Understanding these and other problems and predicting their extent requires knowledge of the thermodynamic properties of Aerozine-50. Unfortunately, much of the data needed to establish these properties does not exist.

On December 27, 1966, a program was undertaken to obtain the needed data and to prepare tables and charts of the desired thermodynamic properties. The program is divided into two phases. The purposes of the first phase are: (1) to accumulate and evaluate data, reported in the literature, for the thermal and physical properties of the pure components, hydrazine and UDMH, and their mixtures; (2) to decide what remaining data must be determined by experiment; (3) to select appropriate techniques for correlating the various data in order to minimize the amount of experi-mentation. The second phase involves the needed experimentation, fitting the data to appropriate equations of state and other correlations, and

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*Unsymmetrical dimethylhydrazine

finally, calculation and presentation of the properties derived from the data.

This report summarizes the results of the first phase of this program.

The data required to calculate values of enthalpy and entropy for Aerozine-50 are discussed in Section 3.0, and the portion of these data which have been found in the literature is discussed in Section 4.0. The proposed correlations of experimental data and techniques for calculating the thermo-dynamic properties from the data are described in Section 5.0. A general description of the experimental procedures and apparatus to be used to obtain the missing data are described in Section 6.0. The presentation of the computed property data is discussed in Section 7.0.

3.0 DATA REQUIRED TO CALCULATE THERMODYNAMIC PROPERTIES

In general, the calculation of enthalpy and entropy for all states may be accomplished from the following data:

1) ideal-gas enthalpy and entropy,

2) equation of state for the vapor and condensed phases,

3) heats of phase transition and mixing,

4) heat capacity, and

5) phase equilibria.

Figure 3-1 is a schematic pressure-temperature diagram for the system Aerozine-50, constructed with the aid of available data. The diagram consists of six single- or multi-phase regions. The condensed phases are separated from the vapor phase by a two-phase region bounded by bubble-point and dew-point curves. The reason for this is that a two-component system generally does not vaporize congruently. Thus, vapor in equilibrium (at the bubble point) with liquid Aerozine-50 does not have the same composition as the liquid, but will have a higher concentration of the more volatile component, UDMH. Similarly, the liquid in equilibrium (at the dew point) with vapor of Aerozine-50 composition is richer in the less volatile component, hydrazine. In between the bubble-point and dew-point curves, the liquid phase has compositions progressing from 100 percent Aerozine-50 to that in equilibrium with gaseous Aerozine-50. An analogous statement holds for the compositions of the vapor.

At high temperatures and pressures the bubble-point and dew-point curves bend over towards each other and meet, forming a loop. The top of this loop corresponds to, or replaces, the critical point of a one-component system. However, the maximum temperature and maximum pressure for the existence of distinct vapor and liquid phases occur at separate points, the plait point and contact point, respectively. Analogous to the condition at the critical point of a single-component system, the enthalpy of vaporization (heat of vaporization) at the contact point is zero.
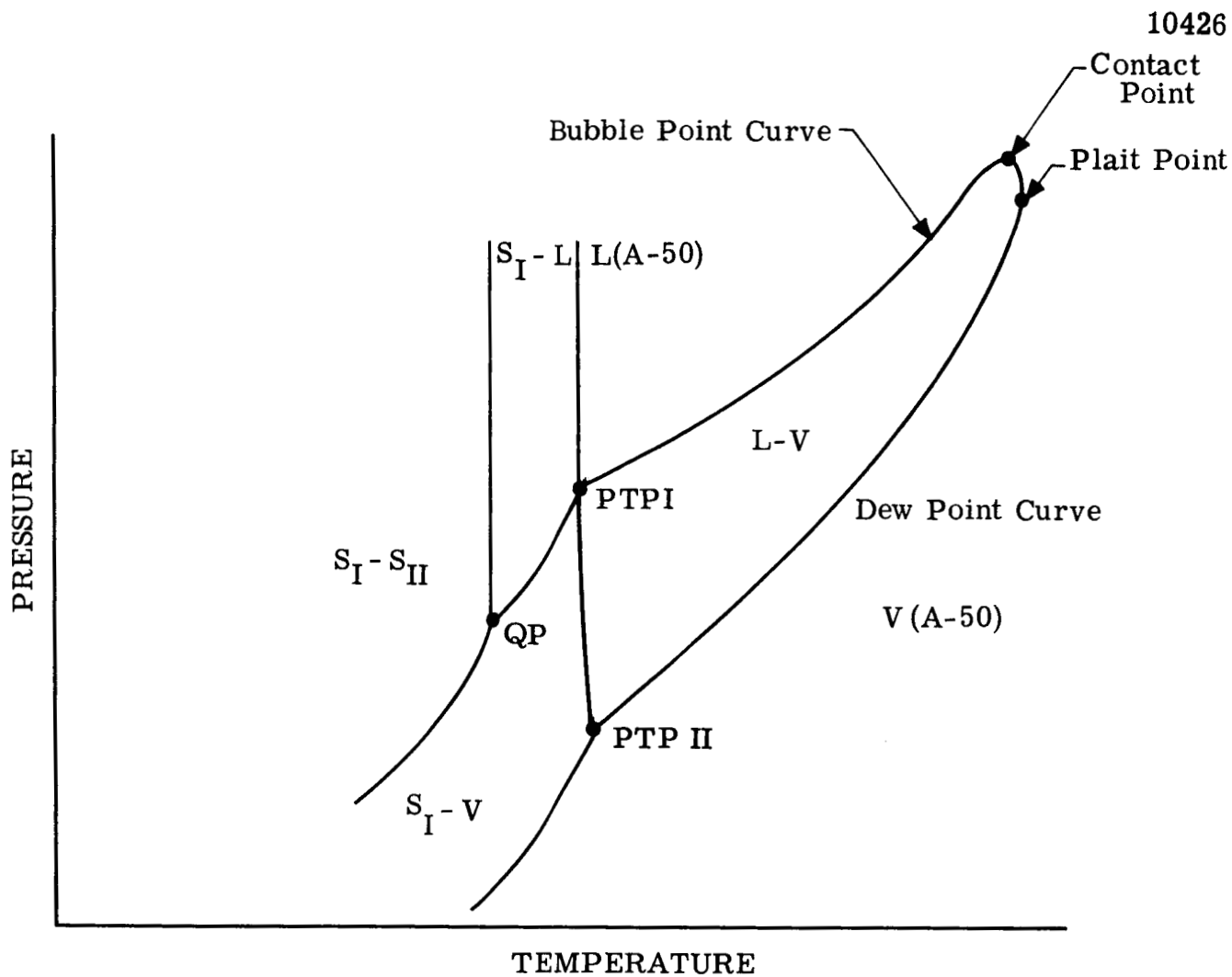
Key:

    V - Vapor

    L - Liquid

    S_I - Solid Hydrazine

    S_{II} - Eutectic (approximately 97% UDMH)

PTPI - Pseudo Triple Point I

PTPII - Pseudo Triple Point II

    QP - Quadriple Point

Figure 3.1. Schematic Pressure - Temperature Diagram
of the System Aerozine-50.

Aerozine-50 does not have a true triple point at which congruent freezing occurs. Instead a "quadruple point" (QP) and two "pseudo-triple-points" (PTP) exist. The first "pseudo-triple-point", PTP-I in Figure 3-1, occurs at approximately -8°C and 30 torrs. Following the vapor-pressure curve from PTP-I to QP, by simultaneously lowering the temperature and pressure of the mixture, S_I(hydrazine) freezes as the liquid becomes en-riched in UDMH. When QP is reached (at approximately -61°C) the liquid has the eutectic composition (approximately 94 per cent UDMH) at which it freezes congruently.

To quantitatively construct this phase diagram, p-T-x data along all of the boundaries of the various regions as well as p-T-x data within these regions are required. Table 3.1 summarizes the data required to calculate values of enthalpy and entropy within the various regions of the phase diagram for Aerozine-50.

In the vapor region, V(A-50), the calculation of enthalpy and entropy requires data for the ideal gas properties of the pure components and an equation of state for the mixture.

In the liquid-vapor region, L-V, values of latent heats of vaporization for the pure components and heats of mixing for the various liquid mixtures as functions of temperature are needed. The latter are related to the activity coefficients of the components of the mixture which are readily calculated from data for phase composition and total pressures. In order to compute the entropy and enthalpy values for each vapor composi-tion equilibrium with the various liquid phases, the composition dependency of the constants of the equation of state for the vapor phase must be known.

In the condensed phase regions, L(A-50), S_I-L, and S_I-S_{II}, heat capacity at constant pressures, heats of phase transition, and ideal-gas property data are needed to calculate enthalpy and entropy values versus temperature. The pressure dependency of these properties in condensed

TABLE 3.1

Data Required for Calculation of
Thermodynamic Properties

Phase Region	Data Required	Data Available
Vapor	p-V-T, Ideal-gas enthalpy and entropy.	Ideal-gas enthalpy and entropy.
Liquid-vapor	p-V-T, Ideal-gas enthalpy and entropy, latent heats of vaporization of pure components, activity coefficients, liquid density, vapor pressure.	Ideal-gas properties, pure component latent heats of vaporization (UDMH limited), vapor pressure (some), and activity coefficient (some), liquid density (some).
Liquid	Density, Heat capacity.	Density (some), heat capacity (some).
Solid-vapor	Vapor pressure, heat of sublimation and density of solid hydrazine, properties of the eutectic mixture, vapor composition or pressure.	Vapor pressure, density of solid hydrazine.
Solid-liquid	Heat capacity, density, liquid composition, heat of fusion, vapor composition or pressure.	Density and heat capacity of solid hydrazine, heat of fusion of hydrazine, vapor pressure of hydrazine, liquid composition.
Solid	Composition, heat capacity, density.	Composition, heat capacity and density of solid hydrazine.

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phases is negligible at pressures well below the critical point.

In addition to these data, liquid and solid phase densities must be available in order to relate the thermodynamic properties to volume.

4.0   DATA AVAILABLE AND EVALUATION

In general, all measurements of properties of hydrazine or UDMH made at high temperatures are suspect since both of these compounds are known to undergo spontaneous, thermal decomposition[1,3,4,5,6]. At lower temperatures, hydrazine is known to be susceptible to heterogeneous or catalyzed decomposition, particularly in the presence of certain metals (including mercury)[15,16]. Even silica will initiate decomposition at certain pressures and temperatures[1,17].

In addition, the purity of the samples used in obtaining the measurements has an influence on the accuracy of the data. In some cases, there was little or no information given about the chemical purity or the preparation of the samples used.

Table 3.1 also summarizes the data which are available for the computation of thermodynamic properties. These data are discussed in the following paragraphs.

4.1   PURE COMPONENTS

4.1.1   Unsymmetrical dimethylhydrazine

Aston et al[8] have reported a value of the ideal-gas entropy of UDMH at 248.16°K equal to 72.82 ± 0.20 e.u, which was calculated from calorimetric data, and a value of 70.70 e.u. for the _trans_ form and 72.30 e.u. for the _gauche_ form, which were calculated from spectroscopic and molecular structure data. The authors state that since the _trans_ form has a higher energy than the _gauche_ form, the _trans_ form exists in negligible quantities at room temperature. Therefore, the agreement between the values of entropy calculated from the two sets of data is very good.

The same authors report an experimental value of 8366 ± 16 cal./mole for the latent heat of vaporization of UDMH at 298.16°k based on calorimetric data and a value of 8353 cal./mole based on vapor pressure data. These agree within about 0.2%. Data for the heat capacity of solid and liquid UDMH were reported in the temperature range from 13° to 287°K.

The vapor pressure of UDMH has been measured by Aston in the temperature range from 237° to 287.16°K, by Pannetier and Mignotte[10] in the range from + 35° to + 65°C, and by Chang and Gokcen[9] in the range from -25°C to +35°C.

The data reported by Aston and coworkers (ideal-gas entropy, heat of vaporization, solid and liquid heat capacity, and vapor pressure) appear to be reliable. From the variation of triple- point temperature with the fraction of sample melted, the solid-insoluble, liquid-soluble impurity was computed to be only 0.01 mole percent. Also, since the measurements were made at or below room temperature, the UDMH probably did not decompose thermally to a significant degree. There is a slight possibility that heterogenous or catalyzed decomposition did occur, however. The calorimeter and the resistance thermometer used for obtaining the data from which the heat capacities were calculated were made of platinum, and the vapor pressures were measured with a mercury manometer. Both of these metals are known to catalyze the decomposition of hydrazine ,and they may cause similar reactions with UDMH.

Chang and Gokcen have reported data for the vapor pressure of UDMH in the temperature range from -25° to +35°C. In general, their data are higher than those reported by Aston, and Pannetier and Mignotte at low temperatures, but are lower at higher temperatures. (Chang and Gokcen made this comparison by extrapolating each of the three sets of data to cover the temperature range from -25° to +75°C). The reason given for differences in the three sets of data is that the test samples employed by Chang and Gokcen were of higher, initial chemical purity. However, they state that the UDMH vapor in their samples may have decomposed due to the presence of the mercury in their manometers.

4.1.2 Hydrazine

Scott et al[7] have reported experimental data for the heat capacity of solid and liquid hydrazine in the temperature range from 12°

to 340°K, the vapor pressure for the solid at 0°C and for the liquid in the range from 0° to 145°C, and the heat of fusion, 3025 cal./mole. The latent heat of vaporization, 10,700 ± 75 cal./mole, was calculated from the vapor pressure data. The ideal-gas entropy at 298.16°K and 1 atmosphere pressure calculated from the calorimetric data is 56.97 ± 0.30 e.u. The value of entropy calculated from spectroscopic and molecular structure data is 57.41 e.u. Free energy, enthalpy, heat capacity, and entropy values were calculated from the spectral and structural data in the temperature range from 298° to 1500°K.

From a study of the melting point as a function of the fraction melted, these authors estimated that their samples used for the calorimetric measurements were 99.75 mole percent hydrazine and that the major impurity was water. They estimate the maximum uncertainty of the values of heat capacity to be 0.3%, resulting primarily from the presence of water in the samples.

The small amount of water in the samples had a more significant effect on the vapor pressure measurements. The authors purified their hydrazine samples further by vacuum distillation, retaining the first 20% to boil over for vapor pressure measurements. They compared their measurements with those reported by Hieber and Woerner[23]. The latter data were consistently lower, and the conclusion was that the hydrazine samples used by Hieber and Woerner contained more water.

Chang and Gokcen reported experimental measurements of vapor pressure over the temperature range from 3° to 52°C. Their data are somewhat higher than those reported by Scott et al and Hieber and Woerner in this temperature interval. They suggested that their data are the most accurate, because they believed that their test samples were more pure than those used by the other investigators. The data of Pannetier and Mignotte, obtained over the range from about 84° to 113°C, were extrapolated to cover the temperature range in which Chang and Gokcen made their measurements. The calculated data were lower, and Chang and Gokcen attribute this fact to the possibility that the samples used by Pannetier and Mignotte contained

a significant amount of water.

4.1.3   General Remarks

Since there are various uncertainties in the data reported for
the pure components, some of the values should be checked experimentally.
It is likely that the data reported for solid and liquid phases at low
temperatures are reliable because decomposition should be slow at reduced
temperatures. However, at higher temperatures the decomposition rates
are higher. As a result, a few measurements of vapor pressure will be
made with both pure components at temperatures somewhat above room tempera-
ture. The apparatus to be used for this will be the same as that used for
measurements with the mixtures, and it will be fabricated from materials
which are inert with respect to both hydrazine and UDMH.

4.2   MIXTURES

Since no p-V-t data for Aerozine-50 vapor have been found in the
literature, it will be necessary to obtain these data by experiment or
analysis. Because of the short period of time allowed for the experimental
portion of this program, only a minimal amount of experimental data will
be accumulated. Interpolation and extrapolation of this data will be
accomplished by employing an appropriate equation of state as discussed
in section 5.1.

The ideal-gas properties of the mixture will be calculated from
the properties of the pure components as discussed in section 5.1.

Chang and Gokcen[9] have studied the liquid-vapor phase equilibria
for mixtures of UDMH and hydrazine in the temperature range from 0° to
20°C. The compositions of the co-existing phases were determined from
measurements of the refractive index of samples of the liquid and condensed
samples of the vapor. In a separate set of experiments, the vapor pres-
sures over liquid mixtures of known composition were measured with a
mercury manometer.

Pannetier and Mignotte[10] reported isobaric data for liquid-vapor

phase equilibria of mixtures in the pressure range from 250 to 760 mm. Phase compositions were determined from measurements of refractive index. The temperature range corresponding to these data was approximately 35° to 112°C.

Chang and Gokcen made a graphical comparison between their pressure-composition data obtained at 20°C and a set of data which they obtained by extrapolating the data of Pannetier and Mignotte to a temperature of 20°C. There was considerable deviation between the two sets of data.

Both of these sets of data, those reported by Chang and Gokcen[9] and those reported by Pannetier and Mignotte[10], were shown to be thermodynamically inconsistent by means of a criterion derived from the Gibbs-Duhem equation by Scatchard and Raymond[9]. In this test, the dew point pressure is calculated from the measured compositions of the equilibrium phases and is compared to the measured pressures. The calculation is made assuming ideal vapor behavior and negligible molar volume of the liquid compared to that of the vapor. These assumptions are reasonable because of the low pressures involved. Since the test applies only at constant temperatures, the isobaric data was converted to isothermal form by cross-plotting.

There are several possible explanations for the inconsistency of these data. The test samples used by the investigators may have decomposed due to catalysis or chemical reaction with the confining vessel or with mercury in the manometers. The samples may have undergone spontaneous, thermal decomposition particularly in the high temperature region in which Pannetier and Mignotte made their measurements.

Another set of p-x-y vapor-liquid equilibria data have been reported by Liberto[14], without reference to the source or to the experimental conditions under which it was obtained.

Because of the various uncertainties in the reported vapor-liquid equilibria data, it will be necessary to obtain new data for the pressure

and temperature regions already investigated. The apparatus to be used for this purpose must be fabricated from materials which do not react with hydrazine and UDMH or catalyze their decomposition. On the other hand it is pointless to attempt measurements at a temperature, above which significant thermal decomposition occurs. This temperature limit remains to be determined.

Data for the density of propellant-grade Aerozine-50 liquid have been reported by Aerojet[12] for the temperature range from 0° to 160°F. These data are averages for various liquid mixtures containing amounts of impurities within the limits of use specifications. As a result, the data exhibit considerable scatter; and, therefore, more consistent data must be obtained by making measurements with pure samples.

Data for the specific heat of propellant-grade Aerozine-50 liquid have been reported by Liberto at two temperatures: 81.2°F and 101.8°F. The data are within 0.5% of the values calculated by Aerojet at the same temperatures. The Aerojet calculations were performed over the temperature range from 21° to 450°F. Since the values of enthalpy and entropy for the liquid will be computed from other kinds of data (heat of mixing, ideal gas properties, etc. (See section 5.0)), the specific heat data discussed above will be used to calculate property values for comparison purposes only. The Aerojet, calculated data should be quite adequate for this purpose, at least at the lower temperatures where they compare favorably with experimental data.

The temperatures and compositions of the condensed phases along the curves PTP-II and PTP-I and PTP-I to QP (see Figure 3.1) have been determined[13,14]. The data reported by McMillan[13] are probably the most reliable, because these investigators prepared their test mixtures from very pure hydrazine and UDMH. They report a eutectic at 94 mole percent UDMH melting at 214°K. (Point QP, Figure 3.1). The point PTP-II has not been determined, nor has the pressure variation along the curves PTP-II to PTP-I and PTP-I to QP.

5.0 CORRELATIONS AND THERMODYNAMIC COMPUTATIONS

5.1 VAPOR REGION

Wilson's modification of the Redlich-Kwong equation of state[18] appears to be well suited for correlating p-V-T data of the vapor phase. This equation is (see Table 5-1, page 5-9, for nomenclature):

$$\frac{pV}{RT} = \frac{V}{V-b} - f\left(\frac{T_c}{T}, \omega\right) \frac{b}{V+b} \quad . \tag{5.1}$$

The constant, b, is independent of temperature and is evaluated from the composition of the vapor mixture and the critical properties of the pure components. Application to Aerozine-50 yields:

$$b_{mix} = 0.0865 \ R \left[\left(\frac{yT_c}{P_c}\right)_h + \left(\frac{yT_c}{P_c}\right)_u\right] \tag{5.2}$$

The coefficient, $f\left(\frac{T_c}{T}, \omega\right)$, is dependent on temperature and Pitzer's acentric factor, ω. For a mixture, f_{mix} is taken to be the molar average of the values for the pure components, which for a mixture of hydrazine and UDMH is

$$f_{mix} = y_h \ f\left(\frac{T_c}{T}, \omega\right)_h + y_u \ f\left(\frac{T_c}{T}, \omega\right)_u \quad . \tag{5.3}$$

For a pure component, f can be computed from the relation

$$f\left(\frac{T_c}{T}, \omega\right) = 4.934 \left[1 + (1.57 + 1.62\omega)\left(\frac{T_c}{T} - 1\right)\right] \quad . \tag{5.4}$$

Values of the acentric factor have been tabulated as a function of reduced temperature.[19]

The validity of this equation of state may be tested by comparison of experimental and calculated values of p-V-T data. If there is

serious deviation then equations 5.1 through 5.4 may still be used, regarding b, T_c and ω as adjustable parameters for curve fitting. For Aerozine-50 and other hydrazine-UDMH mixtures this gives a total of six such parameters.

Once the p-V-T data have been correlated with an equation of state, values of enthalpy and entropy may be computed from the relations,

$$H = H°(T) + f_H(T,p) = H°(T) + PV - RT - \int_{\infty}^{V}\left[P - T\left(\frac{\partial P}{\partial T}\right)_V\right]_T dV \quad (5.5)$$

and

$$S = S°(T) + f_S(T,p) = S°(T) - \int_{P}^{o}\left[\frac{R}{P} - \left(\frac{\partial V}{\partial T}\right)_P\right]_T dP \quad , \quad (5.6)$$

where the integrals are evaluated using the equation of state.

The quantities, $H°(T)$ and $S°(T)$, are the enthalpy and entropy (at unit fugacity) of the ideal gas, respectively, for the vapor mixture and are calculated from the corresponding values for the pure components using the relationships,

$$H°(T) = y_h H°(T)_h + y_u H°(T)_u \quad (5.7)$$

and

$$S°(T) = y_h (S°(T) - R \ln y)_h + y_u (S°(T) - R \ln y)_u \quad . \quad (5.8)$$

5.2 LIQUID-VAPOR REGION

The calculation of enthalpy and entropy values in the liquid-vapor region (Figure 3.1) is a two-part process, since two phases exist in equilibrium. The thermodynamic properties for the vapor phase can be evaluated by the method discussed in the previous section, provided the concentration dependency of the constants of the equation of state have been established.

If it is found that Wilson's modification of the Redlich-Kwong equation accurately predicts the p-V-T data for the vapor region, then the extension of this method into the liquid-vapor region will be straightforward. However, if the constants of the equation must be treated as adjustable, curve-fitting parameters, then additional p-V-T data for UDMH-rich mixtures must be obtained to determine the concentration dependence of the constants.

The thermodynamic properties of the equilibrium liquid phase may be evaluated from the relationships :

$$H_{mix} = x_h \bar{H}_h + x_u \bar{H}_u \tag{5.9}$$

and

$$S_{mix} = x_h \bar{S}_h + x_u \bar{S}_u \; . \tag{5.10}$$

For a component in solution, the partial molal enthalpy and entropy are given by the equations:

$$\bar{H} = H°(T) + f_H (T,p) - \Delta H_v + \Delta H_{mix} \tag{5.11}$$

and

$$\bar{S} = S°(T) + f_S (T,p) - \frac{\Delta H_v}{T} + \Delta S_{mix} \quad , \tag{5.12}$$

respectively. The second terms in each of these equations are defined by equations 5.5 and 5.6, but, in this case they apply to the pure components. The third terms are the enthalpy and entropy of vaporization of the pure components, and the fourth terms are the enthalpy and entropy of mixing.

Enthalpy and entropy of mixing are readily evaluated from composition and pressure measurements if the liquid phase is a regular solution. In this case the enthalpy of mixing for a component in solution is equal to the excess partial free energy and is given by the relation

$$\Delta H_{mix} = RT \ln \gamma \; , \tag{5.13}$$

where γ is the activity coefficient of the component in solution. The entropy of mixing for a regular   solution is the corresponding ideal solution value:

$$\Delta S_{mix} = -R \ln x \quad . \tag{5.14}$$

The activity coefficient for a component in solution may be defined by the relation

$$\gamma_i = \frac{\hat{f}_i}{p_i^o x_i} \quad , \tag{5.15}$$

where p_i^o is the vapor pressure of the pure component, i, at the same temperature. At pressures less than one atmosphere the vapor may be assumed to be ideal and accordingly the fugacity of the component is given by the well known formula

$$\hat{f}_i = p_i = y_i p \quad . \tag{5.16}$$

At higher pressures, ideal behavior cannot be assumed. As a means to account for non-ideality, the often used Lewis and Randall rule may be assumed, and as a result the fugacity of a component is given by the relation

$$\hat{f}_i = y_i f_i \quad , \tag{5.17}$$

where f_i is the fugacity of the pure component at the same total pressure and temperature (often a fictitious state) as the solution. The fugacity may be calculated from data of state for the component, using the formula,

$$RT \ln f = RT \ln p - \int_o^p \left(\frac{RT}{p} - V \right) dp, \tag{5.18}$$

where the integral is to be evaluated at constant temperature.

The corresponding value of the activity coefficient of the second component in the mixture may be computed by means of an integrated form of the Gibbs-Duhem equation :

$$\ln \gamma_2 = - \int_{x_i=0}^{x_i} \frac{x_i}{1-x_i} \, d \ln \gamma_1 \qquad (5.19)$$

The values of the activity coefficients thus obtained must be correlated as functions of temperature and composition to permit accurate interpolation and extrapolation. A common technique for deriving such correlations is to express the excess free energy of mixing as a power series in composition at constant temperature. Since the excess free energy is related to the activity coefficients through equations (5.13) and (5.14), the following equations may be derived:[22]

$$\ln \gamma_1 + x_2 \varepsilon = x_2^2 [B - C(4x_2 - 3) + D(2x_2 - 1)(6x_2 - 5)$$

$$-E(2x_2 - 1)^2 (8x_2 - 7) + \ldots \,], \qquad (5.20)$$

$$\ln \gamma_2 - x_1 \varepsilon = x_1^2 [B + C(4x_1 - 3) + D(2x_1 - 1)(6x_1 - 5)$$

$$+ E(2x_1 - 1)^2 (8x_1 - 7) + \ldots \,], \qquad (5.21)$$

where B, C, D, E, etc, are functions of temperature and ε is defined as

$$\varepsilon \equiv \frac{\Delta V_{mix}}{RT} \frac{dp}{dx_1} \quad .$$

In this definition, ΔV_{mix} is the volume change of mixing, and (dp/dx_1) is the slope of the curve, total pressure versus composition at constant temperature. Ordinarily, ΔV_{mix} is small, and the terms εx_1, and εx_2 are negligible.[22]

5.3 LIQUID REGION

Activity coefficients for the components in liquid Aerozine-50 can be computed by the technique just described. Since the composition of the liquid is invariant throughout this region, only the temperature dependency need be considered. The calculation of enthalpy and entropy is accomplished by using equations (5.9) through (5.12).

5.4 SOLID-VAPOR REGION

Within the solid-vapor region, the composition of the equilibrium vapor phase can be computed from the total pressure and the vapor pressure of solid hydrazine,

$$p = p_h^o \left(1 + \frac{y_u}{1-y_u} \right) , \tag{5.22}$$

where y_u is the mole fraction of UDMH in the vapor and p_h^o is the vapor pressure of solid hydrazine. At the solid-vapor, vapor boundary, the vapor composition is that of Aerozine-50 (0.348 mole percent UDMH and 0.652 mole percent hydrazine), and application of equation (5.22) yields the formula,

$$p = p_h^o \left(1 + \frac{0.348}{0.652} \right) . \tag{5.23}$$

Therefore the dew point curve for this region can be calculated from the data for the vapor pressure of hydrazine, alone.

Since only solid hydrazine is present, the pressure variation along the curve connecting points QP and PTPI, in Figure 3.1, can be computed from the relationship

$$p = p_h^o + \gamma_u p_u^o x_u , \tag{5.24}$$

where γ_u is given by one of the equations (5.20) or (5.21). The required values of x_u have been determined experimentally (Section 4.2). Because

the total pressure is low along this curve, the vapor has been assumed to
be ideal. The curve from PTPI to PTPII represents the freezing of the
partially condensed vapor to form solid hydrazine. The composition along
this curve is therefore defined by the condition $\gamma_h = 1$, which if introduced
into equations (5.20) and (5.21) permits calculation of the composition.
Substitution of these values into equation (5.24) gives the pressure along
this curve. Moreover it may be shown that the temperature corresponding
to PTPII is the freezing point of pure hydrazine, 34.7°F, and the pressure
computed from equation (5.23) is 7.6 torr.

The curve extending downward and to the left of QP in Figure 3.1
represents the sum of the vapor pressures of hydrazine (SI) and the eutectic
(SII). Since the latter is 94 mole percent UDMH, the curve is very nearly
identical with the sum of the vapor pressures of solid hydrazine and solid
UDMH.

The values for enthalpy and entropy of the vapor in this region
may be computed by the techniques described in Section 5.1. The enthalpy
and entropy of solid hydrazine are given by the formulas:

$$H_h(\text{solid}) = H°(T) - \Delta H_{sub} \tag{5.25}$$

and

$$S_h(\text{solid}) = S°(T) - \frac{\Delta H_{sub}}{T} + R \ln p_h^o \quad, \tag{5.26}$$

where, again, the vapor has been assumed to be ideal because of the low
pressures involved. The thermodynamic properties of the eutectic may be
estimated from similar formulas.

5.5 SOLID-LIQUID

The enthalpy and entropy of the liquid phase may be computed from
equations (5.9) through (5.12) according to the techniques discussed in
Section 5.2. The corresponding values for the solid phase, hydrazine, may

be computed from equations (5.25) and (5.26).

The composition of the liquid within this region may be computed from the requirement that the partial molar free energies of the hydrazine in solution and in the pure - solid phase are equal. From equations (5.11) through (5.14) it may be shown that this requirement reduces to the relationship

$$\gamma(T,x) = \frac{1}{x} \quad . \tag{5.27}$$

Assuming that the correlations derived for the activity coefficients in the liquid-vapor region are valid in this region, also, equation (5.20) together with equation (5.27) permit the calculation of composition at any given temperature.

5.6 SOLID REGION

Since the composition of the eutectic, SII, is known, a technique similar to that discussed in the previous section may be used to establish the SI – SII, SI – L boundary and to calculate the desired values of enthalpy and entropy in the SI – SII region.

TABLE 5.1

NOMENCLATURE

F -   Free energy, BTU/lb-mole

f -   Fugacity, psia

H -   Enthalpy, Btu/lb-mole

H° -   Ideal gas enthalpy, Btu/lb-mole

p -   Pressure, psia

p_c -   Critical pressure, psia

p° -   Vapor pressure, psia

R -   Universal gas constant, 1.987 Btu/lb-mole $^{\circ}$F

S -   Entropy, Btu/lb-mole $^{\circ}$F

S° -   Ideal gas entropy, Btu/lb-mole $^{\circ}$R

T -   Temperature, $^{\circ}$F

T_c -   Critical temperature, $^{\circ}$F

y -   Vapor composition, mole fraction

x -   Liquid composition, mole fraction

V -   Molar volume, cu.ft./mole

γ -   Activity coefficient, defined by equation (5-15)

NOMENCLATURE (Continued)

Superscripts

 bar $\bar{(\;)}$ indicates partial molar quantity

Subscripts

 h - hydrazine

 u - unsymmetrical dimethylhydrazine (UDMH)

 H - enthalpy function

 S - entropy function

6.0 PROPOSED EXPERIMENTS AND APPARATUS

It is clear from the discussion in sections 3.0 and 4.0 that much additional data must be determined in order to compute the thermodynamic properties of Aerozine-50. The additional measurements which are required and the experimental techniques presently planned to perform these measurements are discussed in the following subsections. The experimental effort will consist of the measurement of the p-V-T properties of the vapor, the density of the liquid phases, and vapor-liquid equilibria. Most measurements will be made at pressures below three atmospheres. When necessary to confirm correlations for the data, a few additional measurements will be made at pressures between three to twenty atmospheres.

6.1 PROPOSED EXPERIMENTS

6.1.1 Vapor Region

Since the ideal gas properties of hydrazine and UDMH are available, only p-V-T data for A-50 vapor must be obtained. It is planned to determine these data using the constant-volume vessel shown schematically in Figure 6.1. The adjusted variables will be temperature (controlled by a thermostated bath or oven) and specific volume (determined by the measured weight of charge in the vessel). The pressure corresponding to a given set of these fixed conditions is the dependent variable.

The data obtained will be used to check the applicability of the Redlich-Kwong equation of state, equation (5.1), in which actual or estimated values of T_c, ω, and b for the components are used. For this purpose, it is planned to make a series of four measurements of pressure versus specific volume along a high-temperature ($\sim250°F$) isotherm. If the data prove the equation to be inapplicable in this form, then similar measurements along two additional isotherms will be performed to permit correlation of the data of state in the same form as the Redlich-Kwong equation.

In order to determine the variation of the constants for the resulting equation (or correlation) with the composition, similar measurements will be repeated with UDMH-rich vapors, at two compositions.

6.1.2   Vapor-Liquid Region

The vessel employed in obtaining the p-V-T measurements will be so designed that it may be used for performing the phase equilibria experiments also. The experiments will involve measuring the total vapor pressure and the phase compositions corresponding to various values of temperature.

These data together with equation (5.15) will be used to calculate values of γ as a function of temperature and composition. The resulting γ-x data will be correlated by means of equations (5.21) and (5.22). It is expected that only three terms of the series in equations (5.21) and (5.22) need be retained and that the constants are linear functions of temperature. Therefore, a series of nine experiments are planned, involving three values of liquid composition at each of three temperatures.

6.1.3   Liquid Region

The density of A-50 liquid will be determined as a function of temperature by weighing the liquid required to totally fill a small vessel of known volume. Four such measurements are planned, since liquid density is ordinarily a quadratic function of temperature over a rather wide range. Similar measurements are planned for hydrazine-rich solutions in order to determine the volume of compositions in the liquid-vapor region.

6.2   APPARATUS AND PROCEDURE

As presently planned, the experiments to determine p-V-T properties and vapor-liquid equilibria will be performed in an apparatus consisting of a constant volume cell, a constant temperature bath, sample traps and a charge vessel. The arrangement of these components, together with the associated instrumentation for the experiments, are shown schematically in Figure 6-1.

The constant volume cell is to be a thick-wall vessel and will be constructed from 6061-T6 aluminum or some other alloy which proves to be compatible with UDMH-hydrazine mixtures. (Planned experiments to demonstrate
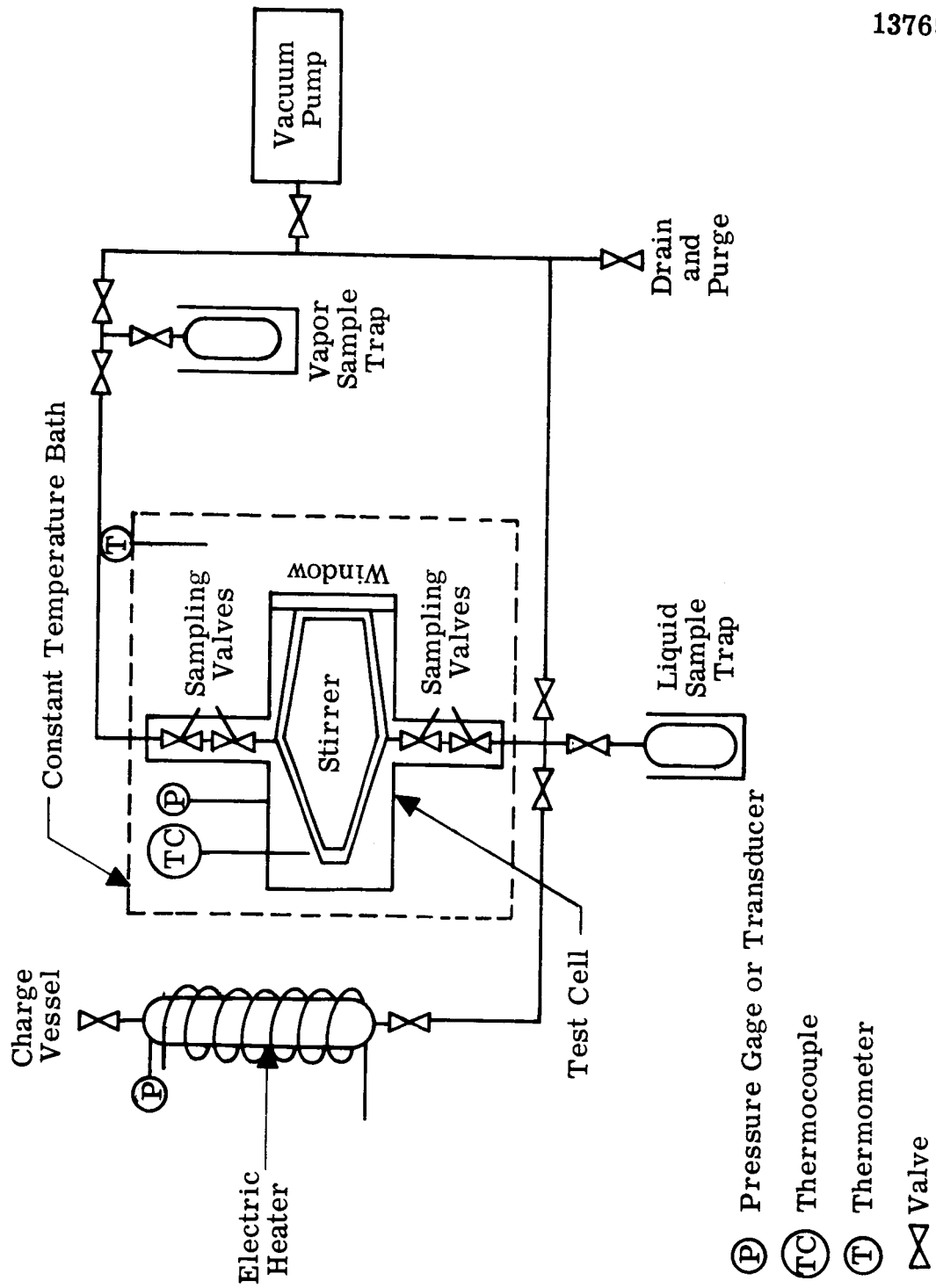
Figure 6.1. Apparatus for PVT and Equilibrium Experiments.

compatibility are described in Section 6.5). The cell will have a Pyrex window at one end to permit visual observation of the phases present. In order to insure the establishment of equilibrium, the contents of the cell will be stirred by a flat, magnetically driven paddle, which revolves about the horizontal (long) axis and sweeps the entire volume of the cell. The sampling valves are to be inserted in the walls of the cell in order to minimize the unstirred spaces between the interior of cell and the valve seats.

The pressure of the contents of the cell will be measured with a variable reluctance-type transducer which has a minimum resolution of about 0.057 torr. During the low-temperature experiments, this transducer will be mounted on the outer surface of the cell and will be connected to the vapor space in the cell through a small-diameter port drilled through the wall. To protect the transducer during the experiments at higher temperatures, the transducer will be mounted outside of the bath (Figure 6.1). In this case, pressure will be sensed through an oil-filled line and a diaphragm, in the cell wall, which separates the oil and contents of the cell.

The transducer will be calibrated directly with standard pressure gages such as a McLeod-type vacuum gage, Bourdon-tube pressure gages, open-end U-tube manometers, etc. When the transducer is to be used with an isolating diaphragm and oil filled line, the entire assembly will be calibrated as a unit.

The temperature of the cell will be controlled by immersing it in a thermostated bath whose temperature will be measured with a calibrated thermometer. Several thermocouples, which will be imbedded in the thickest portions of the wall of the cell, with their beads located very near the inner surface, will be used to check the establishment of thermal equilibrium throughout the cell.

Prior to charging the constant-volume cell, the entire system of cell, sample traps, charging vessel and connecting lines (Figure 6-1) will be purged with ultra-pure nitrogen gas and then evacuated to a pressure of about 0.01 torr. The charging vessel will be filled with the desired liquid,

weighed on an analytic balance and then connected to the system. The cell will be filled with liquid to the desired level by opening the appropriate valves and heating the charging vessel (if necessary) until the vapor pressure of the liquid contents exceeds the pressure in the cell. The weight of material charged into the cell will be determined by freezing and then re-weighing the charging vessel.

The experiments will be conducted by adjusting the bath temperature to the desired value and then waiting until equilibration of the temperature and pressure in the cell has been achieved. Then samples of the various phases (if more than one) will be withdrawn for quantitative, chemical analysis. At this point, one experiment is complete. Another experiment may be conducted by changing the temperature or by the addition (or removal) of liquid. A complete inventory of liquid charged and removed will be maintained in order that the total mass of hydrazine and UDMH in the cell is known for each experiment.

6.3 PREPARATION AND PURIFICATION OF UDMH AND HYDRAZINE

At present, it is believed that sufficient purification can be accomplished by a simple batch distillation of the commercially available hydrazine and UDMH. A flow diagram of a suitable distillation apparatus for this purpose is shown in Figure 6.2. In operation, the system is purged with ultra-pure nitrogen, and then the pressure is lowered enough to draw a charge into the boiler through the filling line. A trap to collect the product is immersed in a bath whose temperature is slightly higher than the freezing point of the product. A "light-ends" trap is immersed in a liquid nitrogen trap and accordingly only the permanent gases will leave the system.

To perform the distillation, the boiler is immersed in a warm water bath and the pressure of the system is lowered until boiling occurs. During the distillation, the temperature of the warm water bath and the cold bath are carefully maintained to minimize the need for regulating pressure.

To date, propellant-grade hydrazine has been distilled in a crude version of this system. Gas-chromatographic analyses indicated that a single distillation produced a significant reduction in the concentration of
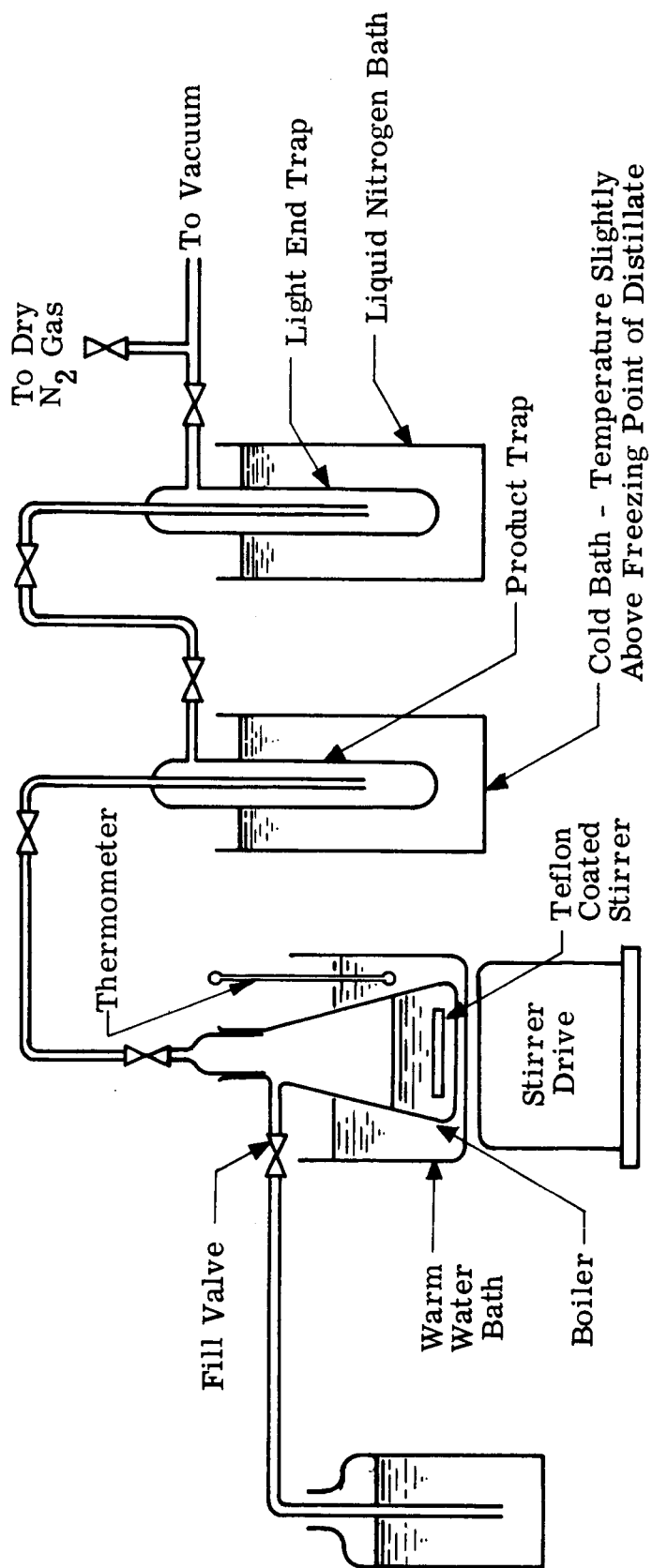
Figure 6.2. Vacuum Distillation Apparatus for Purifying Hydrazine and UDMH.

impurities, including water and amines. Consequently, it appears that hydrazine of sufficient purity can be obtained by a single distillation. Similar results are expected for UDMH.

6.4 ANALYSIS OF SAMPLES

The analysis of the liquid and vapor samples probably will be performed by means of gas chromatography. A column for separating hydrazine and UDMH mixtures already has been developed. With proper calibration, a resolution of 0.001 mole fraction can be achieved.

6.5 DECOMPOSITION STUDIES

As indicated in Section 3.0, both hydrazine and UDMH are susceptible to homogeneous and heterogeneous decomposition. Therefore, a few stability tests are to be performed in order to determine their compatibility with candidate materials for the construction of the experimental apparatus.

The apparatus to be employed for this purpose is shown diagrammatically in Figure 6.3. It consists of a heated pressure vessel, which will contain the samples of the candidate materials and the fuel mixture. To perform the experiments, the samples will be placed in the vessel. Next, the entire system will be purged with nitrogen gas, evacuated to a pressure of approximately 0.01 torr, filled to half-full with the fuel mixture under its own vapor pressure, and then sealed by closing the appropriate valves. The vessel will then be removed from the system, wrapped in an electric heating mantle, and heated to a given temperature while carefully monitoring the pressure. The vessel and its contents will be held at this temperature for about four hours. During this period, the pressure will be recorded at various times (an increase in pressure at constant temperature is an indication of decomposition of the fuel). At the end of this period, the mantle will be removed, permitting the vessel to cool until the pressure is low enough to safely extract liquid and vapor samples. These will be analyzed for decomposition products (ammonia and amines).
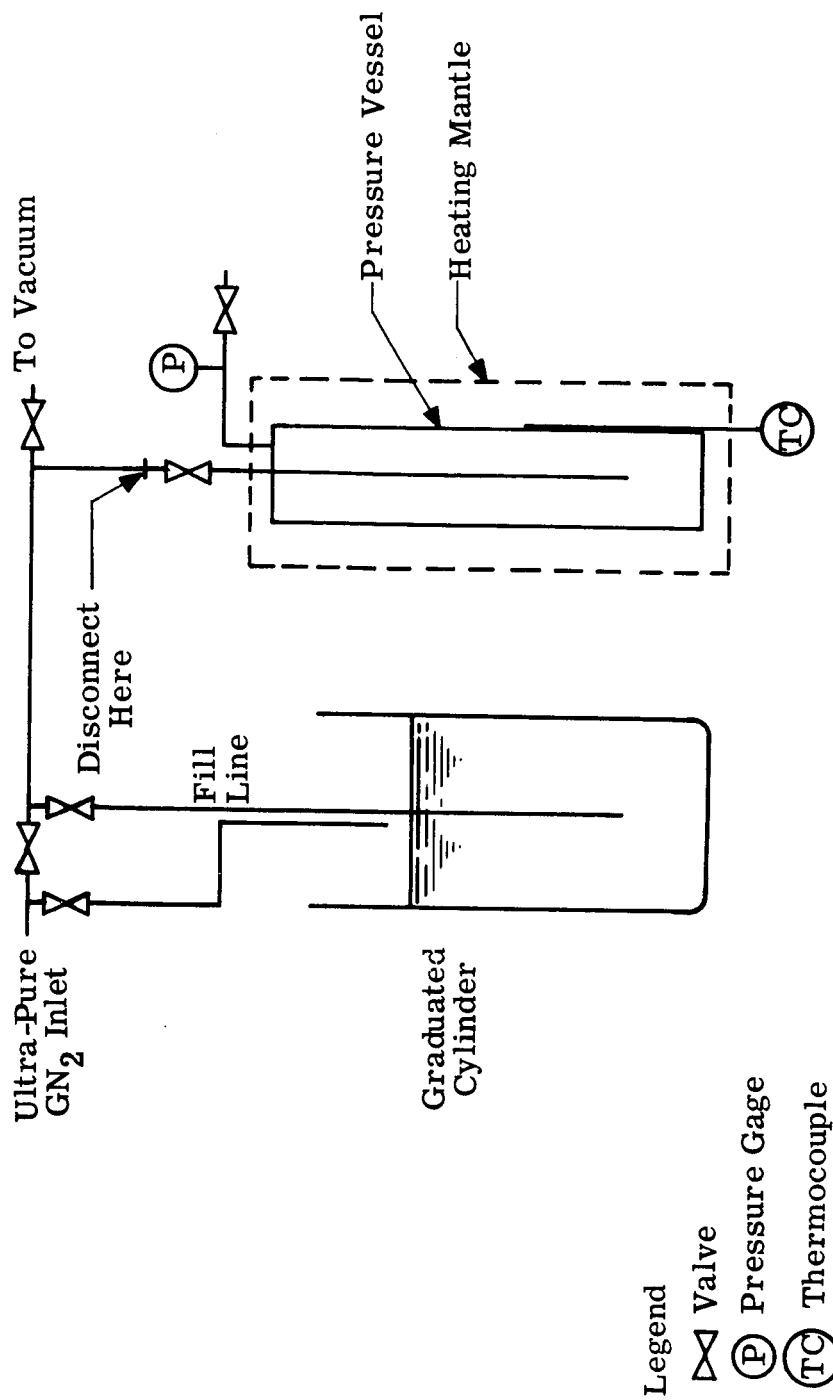
Figure 6.3. Apparatus for Stability Determinations.

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At present, it is planned to test the following candidate materials:

(1) TFE Teflon

(2) 304 and 316 stainless steel

(3) Pyrex

(4) 6061-T6 aluminum.

On the basis of information found in the literature,[20] these materials appear to be the least reactive with hydrazine compounds.

7.0   PRESENTATION OF PROPERTY DATA

Detailed tabulations of the thermodynamic property values will be made, indicating corresponding pressures, temperatures, and phase compositions. Sufficiently small intervals will be used to permit accurate, linear interpolation between tabulated values. In addition, skeletal pressure-enthalpy, temperature-entropy and pressure-temperature diagrams will be presented. All of these data will be reported in standard engineering units (Btu, °F, psia, and weight fractions, etc.).

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