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Literature Survey

DETERMINATION OF PROPERTIES OF FLUIDS FOR SOLAR-COOLING APPLICATIONS

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LIST OF SYMBOLS AND UNITS

The following symbols and units are used in this report.

Symbol	Units	Definition
c_p	cal mol^{-1} K^{-1}	Heat capacity at constant pressure
c_σ	cal mol^{-1} K^{-1}	Heat capacity of pure liquid at saturation
c_ℓ (w)	cal mol^{-1} K^{-1}	Heat capacity of liquid mixture at weight fraction w
H_m (w)	cal mol^{-1}	Heat of mixing at weight fraction w
P	atm	Vapor pressure of pure fluid
P_c	atm	Critical pressure
T_b	K	Boiling point temperature at 1 atm
T_c	K	Critical temperature
T_m	K	Melting point temperature at 1 atm
T_b (x)	K	Bubble point of fluid mixture at mole fraction x
T_D (x)	K	Dew point of fluid mixture
v_c	cm^3 mol^{-1}	Critical volume
v_g	cm^3 mol^{-1}	Specific volume of saturated vapor
v_ℓ	cm^3 mol^{-1}	Specific volume of saturated liquid weight fraction
w	---	Weight fraction
x	---	Mole fraction
ΔH_v	kcal mol^{-1}	Heat of vaporization of normal boiling point
°	---	Ideal gas reference state (superscript)
(spect)	---	Calculated from spectroscopic data

INTRODUCTION

The Department of Energy has funded the development of solar-powered absorption air conditioning technology, in which solar power provides the heat for evaporating the refrigerant from a refrigerant/absorbent solution. The principle is similar to that used in gas or propane refrigerators. In the currently used devices, the refrigerant/absorbent pair is ammonia/water. Other refrigerant/absorbent pairs have been suggested to improve the efficiency of these devices, but they have not been tested because of a lack of adequate thermodynamic and thermal stability data.

The objectives of this project were to perform a detailed literature search for the available thermodynamic data of proposed refrigerant/absorbent pairs (pure fluids and binary fluid mixtures; see Tables 1 and 2) and to measure those data that are unmeasured or unreliable. The data to be obtained for the pure fluids included the critical temperature, pressure, and volume; the vapor pressure curve; the latent heat of vaporization at the normal boiling point; the freezing point; the specific heat of the liquid and vapor; and the specific volumes of the saturated liquids and vapors. For the fluid mixtures, the data included the dew point and bubble point at four specified pressures plus the heats of mixing and specific heat at several solution compositions. The specific data of interest for this survey are listed below.

- Pure Fluids
  - The pressure (P_c), temperature (T_c), and volume (v_c) at the critical point
  - The vapor pressure at T_1, T_2, T_3, and T_4 where

    $0.84\ T_c < T_1 < 0.86\ T_c$

    $0.69\ T_c < T_2 < 0.71\ T_c$

    $0.59\ T_c < T_3 < 0.61\ T_c$

    $0.49\ T_c < T_4 < 0.51\ T_c$

Table 1

PURE FLUIDS INCLUDED IN SURVEY

Refrigerants	Absorbents
Ammonia	Ethylene glycol
Methylamine	1,4-Butanediol
Ethylamine	Diethylene glycol dimethyl ether (DGDE)
Chlorodifluoromethane (R-22)	N,N-dimethylacetamide (DMA)
Fluorodichloromethane (R-21)	N,N-dimethylhexanamide (DMH)
	N,N-dimethyldecanamide (DMD)

Table 2

BINARY FLUID MIXTURES INCLUDED IN SURVEY

Ammonia/ethylene glycol
Ammonia/1,4-butanediol
Methylamine/ethylene glycol
Methylamine/1,4-butanediol
Ethylamine/ethylene glycol
Ethylamine/1,4-butanediol
R-22/DGDE
R-22/DMA
R-22/DMH
R-22/DMD
R-21/DGDE
R-21/DMA
R-21/DMH
R-21/DMD

  - The normal boiling point, T_b
  - The melting point, T_f
  - The latent heat of vaporization at T_b
  - The specific heat of the saturated liquid at T_1, T_2, T_3, and T_4
  - The specific heat of the vapor at a pressure less than 1 atm and at T_1, T_2, T_3, and T_4
  - The specific volume of the saturated liquid and the saturated vapor at T_1, T_2, T_3, and T_4

- Fluid Mixtures
  - The saturation temperatures for two mixtures: one at a mole fraction of 0.35 and the other at a mole fraction of 0.1 of the refrigerant at the vapor pressures P_1, P_2, P_3, and P_4, where P_1 is the vapor pressure of the pure refrigerant at T_1.
  - The heats of mixing, H_M, at 25°C for the mixtures of 0.1, 0.2, 0.5, and 0.8 weight fraction of the refrigerant.
  - The specific heats of liquid mixtures of weight fractions 0.1, 0.2, and 0.5 of refrigerant over the temperature range from the saturation temperature of the mixture at P_1 to the saturation temperature of the mixture at P_4 or to 25°C, whichever is smaller.

In addition, we evaluated the reliability of the data. The following accuracy limits were used to judge data reliability:

- Fluid purity: 99.7%
- Absolute pressures, volumes, latent heats, specific heats: ±1%
- Temperatures: ±0.25°C
- Mole concentrations: ±1%
- Heats of mixing: ±2%.

This report summarizes the results of the literature search, which is Task 1 of this project.

THERMODYNAMICS

This section describes the thermodynamic quantities measured, as well as the experimental methods used and the measurement uncertainties.

The critical point is the fluid state at which the densities of the co-existing vapor and liquid phases are equal, and is also the highest temperature and pressure at which $(\delta P/\delta V)_T$ is zero. Thus the critical temperature (T_c), critical pressure (P_c), and critical volume (v_c) are most often measured by either of two methods:[1]

(1) Observing the temperature, pressure, and volume at which the meniscus vanishes in a system maintained at an overall density approximately equal to the critical.

(2) Making large-scale plots of P-V isotherms up to the critical temperature.

If the precision required of the T_c determination is ±0.1K or more, then it does not matter which method is used nor does it matter whether the sample tube is filled exactly to the critical density. The critical volume is usually determined by the law of rectilinear diameters.[2] The critical pressure is obtained either directly at the observed T_c, or from the P-V isotherm. The critical pressure is usually corrected by subtracting the vapor pressure of pure mercury vapor at T_c. More precise determination of P_c (to ±0.02 atm) requires corrections for hydrostatic and gravitational effects.[3]

The vapor pressure of a pure fluid is given directly by the tie-line[*] between the bubble point, or specific volume of the liquid at saturation (v_ℓ), and the dew point, or specific volume of the vapor at saturation (v_g), on the P-V isotherm (see Figure 1).

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[*] The lack of inflection in the P-V isotherm below T_c is a sensitive indication of fluid impurity.

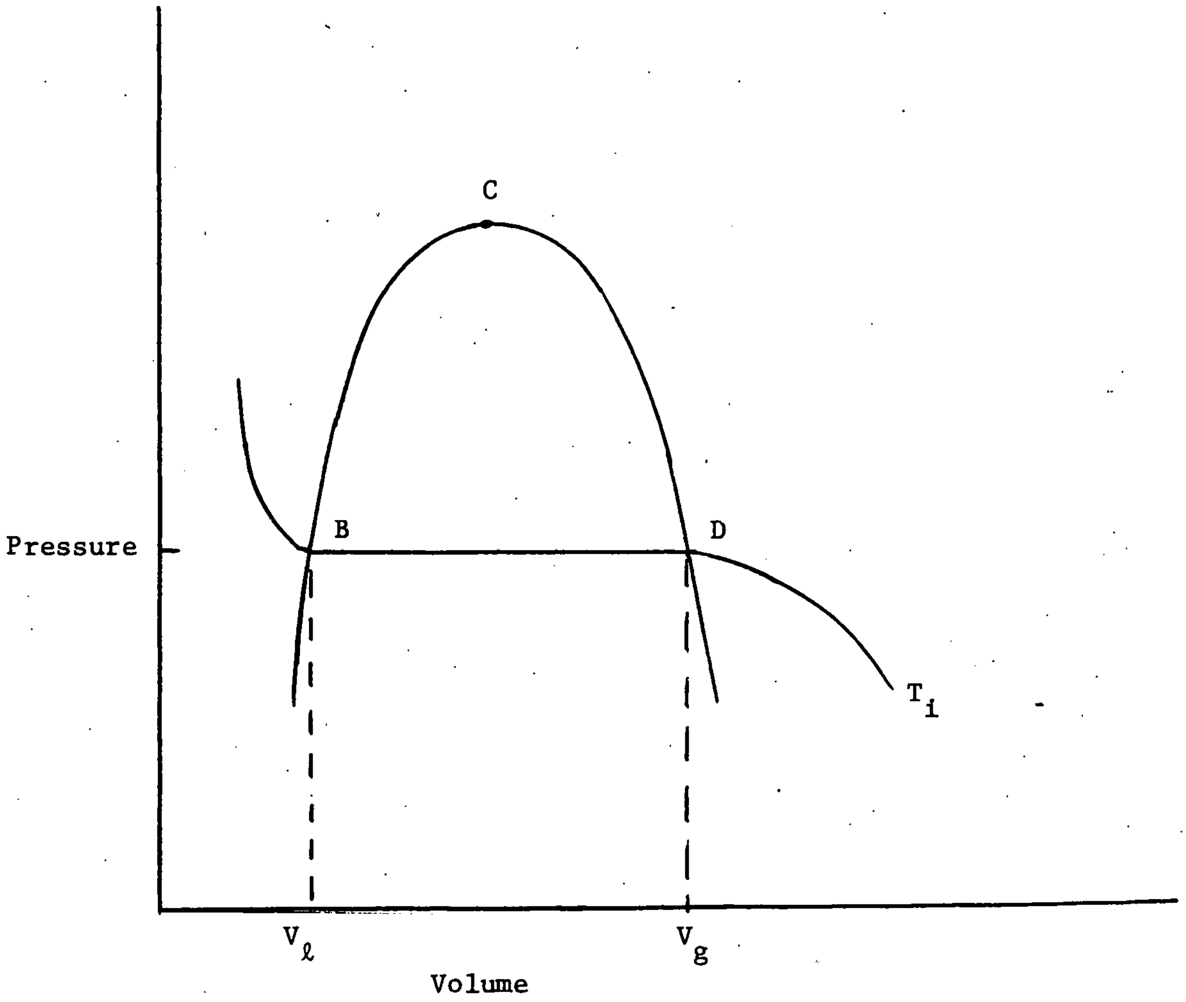

FIGURE 1 SATURATION CURVE AND P-V ISOTHERM AT TEMPERATURE T_i FOR A PURE FLUID. B is the bubble point, D is the dew point, and C is the critical point.

To determine the critical properties, vapor pressures, and specific volumes of the pure fluids to the accuracy required in this project we must achieve the following:

(1) The temperature of the sample must be controlled and measured with an accuracy better than ±0.25 K.

(2) The pressure must be measured with an accuracy better than ±1% and must remain constant in the two-phase region.

(3) The volume V and mass m of the fluid must be measured with uncertainties ΔV and Δm such that

$$\left|\frac{\Delta V}{V}\right| + \left|\frac{\Delta m}{m}\right| < 0.01$$

The normal boiling point of a pure fluid is simply the temperature at which the vapor pressure of the fluid is 760 torr. To meet the required accuracy of 0.25 K, it is necessary that

$$\left|\Delta P \left(\delta T/\delta P\right)_{\sigma}\right| + |\Delta T| < 0.25$$

where ΔP and ΔT are the error limits of the pressure and temperature measurements and σ refers to the saturation curve.

The melting or freezing point of a pure substance is the temperature at which the solid and liquid phases are in equilibrium at atmospheric pressure. Most measurements of the freezing point involve slowly cooling the fluid and noting the onset of crystallization either visually or calorimetrically by the evolution of the heat of fusion.

The heat capacity of the vapor at a pressure of less than 1 atm may be measured at constant volume (c_v) or constant pressure (c_p). c_v is usually measured by comparing the heat capacity of a calorimeter with and without a sample of fluid. The direct measurement of c_p is usually achieved by a continuous flow method. At low pressures, c_p equals the heat capacity of the ideal gas, c_p^o, which may also be calculated spectroscopically. However, the spectroscopic calculation of c_p^o becomes cumbersome and more inaccurate as the number of atoms, and hence the number of internal degrees of freedom in the fluid molecule, increases.

The uncertainty in direct measurements of vapor heat capacity is usually caused by the uncertainty in the amount of heat added to the sample that leaks to the environment and the uncertainty of measuring the difference between the initial and final temperatures of the heated samples. The inherent uncertainty of heat capacity measurements usually requires great experimental care and replicate measurements to assure less than 1% uncertainty.

None of the three heat capacities c_v, c_p, or c_σ can conveniently be measured directly for a saturated liquid.[2] A direct measurement of c_v is difficult at temperatures below the critical point because of the problem of confining the liquid to constant volume as the temperature is raised. The direct measurement of c_p of a saturated liquid is impossible because heat input at constant pressure simply evaporates the liquid. c_σ, which is equal to the amount of energy supplied per unit rise of temperature to heat a liquid along its saturation curve, can in principle be measured directly. This measurement would require adjusting the volume of the calorimeter to that of the saturated liquid, which would be difficult to accomplish experimentally.

In practice, it is customary to measure the heat capacity at constant total volume of a liquid in equilibrium with a small amount of its vapor. This total heat capacity C may be related to c_σ by:[2]

$$C = m\, c_\sigma - T\gamma_\sigma v_\ell \alpha_\sigma + m_g T \Delta v \left(\partial^2 P/\partial T^2\right)_\sigma \tag{1}$$

where m is the total number of moles, subscript σ refers to the saturated liquid, subscripts ℓ and g refer to the liquid and gas phases, T is the temperature, v is the molar volume, P is the vapor pressure, and

$$\alpha_\sigma = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_\sigma$$

$$\gamma_\sigma = \left(\frac{\partial P}{\partial T}\right)_\sigma \tag{2}$$

$$\Delta v = v_g - v_\ell$$

Thus by knowing the amount of vapor in the calorimeter and P-V-T data at the required temperature, we can calculate the specific heat of the saturated liquid from the measured total heat capacity C. At low vapor pressures and volumes, the difference between C and mc_σ is negligible. At higher vapor pressures, these corrections become more important.

A number of workers[3,4] have demonstrated that heat capacity values for liquid systems can be accurately obtained to 1% or better using simple apparatus such as adiabatic calorimeters or commercial differential scanning calorimeters.[5]

Heats of vaporization (ΔH_v) are usually evaluated either by direct calorimetric measurement of the amount of heat necessary to vaporize a known amount of material or by calculation using the Clausius-Clapeyron equation from measurements of the change of vapor pressure with temperature:

$$\Delta H_v = T\Delta v\left(\frac{\delta P}{\delta T}\right)_\sigma \qquad (3)$$

where $\Delta v = v_g - v_\ell$. Many experimental values of ΔH reported in the literature have, in fact, been calculated from equation (3).

Whereas the saturation temperatures of a pure fluid at the dew point and bubble point are equal, the corresponding isobaric saturation temperatures of a binary fluid mixture are not. As shown in Figure 2, the dew point of a mixture is always greater than the bubble point. Thus, in contrast to pure fluid measurements, for binary fluid mixtures care must be taken to measure the saturation temperatures at exactly the dew point and the bubble point.

If two liquids are mixed and the enthalpy of mixing (H_m) is positive, there will be a lowering of temperature under adiabatic conditions. If H_m is negative, then the mixture warms on adiabatic mixing. A second experiment is then conducted to determine the amount of heat needed to produce such a lowering or rise in the temperature. The difficulties are the usual ones in adiabatic calorimetry: minimizing heat leaks to the surroundings, ensuring rapid and sensitive thermometry, minimizing vaporization, and ensuring satisfactory stirring. In addition, if the

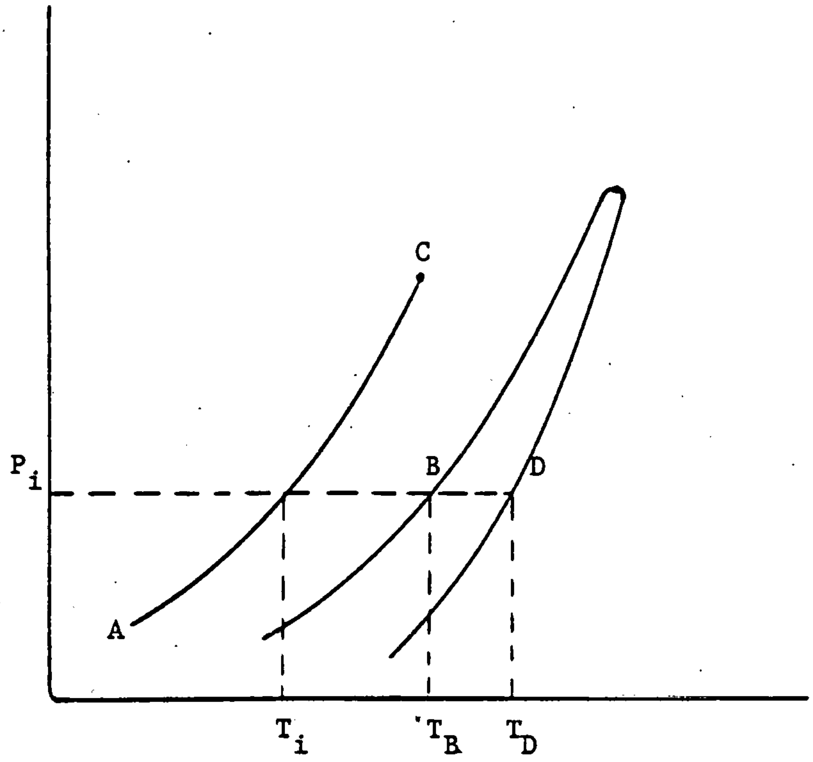

FIGURE 2 Pressure-temperature (P-T) curves for fluids Curve AC is for the pure saturated refrigerant. The curve containing points B and D is for a saturated refrigerant/absorbent mixture. T_B and T_D are the bubble point and dew point temperature, respectively, of the mixture at the pressure P_i.

temperature change (ΔT) for adiabatic mixing is large, then the measured heat of mixing differs from that at the initial temperature by approximately

$$1/2 \left(\frac{\delta H_m}{\delta T}\right)_p \Delta T$$

This difficulty may be overcome if H_m is positive by a simultaneous supply of heat during mixing to maintain a constant temperature.[6] If H_m is negative, the rise in temperature may be minimized by removing a calibrated amount of heat by a thermoelectric cooling device.[7]

SURVEY RESULTS

The literature survey has benefited the experimental program for this project in several respects. First, it has reduced the amount of work to be performed in that reliable literature data for approximately half of the pure fluid measurements have been found. Second, the accurate data found will be used as calibration standards to check the reliability of experimental methods to be used. Finally, estimation methods found in the literature have enabled us to estimate unmeasured data and thereby refine our experimental protocols. For example, many of the estimated vapor pressures of the pure absorbents at $T_r = 0.5$ are less than 1 torr, at temperatures greater than 25°C, and this necessitated adding a Baratron to our pressure measuring apparatus.

The scientific literature survey was conducted on the Scientific and Technical Information files (STIF) of NASA through the center at the University of Southern California. In addition, Chemical Abstracts and the National Technical Information Service (NTIS) files were searched by means of DIALOG, a computerized file, back to 1964. Older literature sources were searched manually. Finally, major chemical manufacturers, such as DuPont, Dow, and Union Carbide, were consulted.

Criteria for Data Reliability

The criteria for assessing the reliability of experimental data were:

- Sample purity
- Sensitivity and calibration of the measuring instruments
- Calibration standard of a reference compound for which accurate literature values are known
- Comparison with other published measurements
- Reliability of the investigator.

Initial screening based on the purity criterion eliminated many of the values. Attention was given to the source and/or method of synthesis of the sample as well as the number and kinds of purification procedures used. Estimations of sample purity were made in some cases by comparing the simple physical properties, such as refractive index or boiling point, with well-established literature values. Close attention was also given to the method of measurement and the sensitivity and calibration of the measuring instruments. The reliability of measurements was greatly enhanced if the investigation included a reference compound for which the determined value closely approximated a well-established literature value. Furthermore, if a set of experimental values from different investigators spanned a range less than the required uncertainty of measurement, all of those values were judged reliable. Finally, greater weight was given to the reliability of data gathered by an investigator with a good reputation for accurate work.

Pure Fluid Data

Refrigerants

Ammonia. The excellent and exhaustive review by Davies[8] was used to determine reliable thermodynamic data for ammonia. These data are listed in Table 3[*] together with the references given by Davies. The critical constants are those taken from a review by Pickering.[9] The normal boiling point of 239.76 K is taken from a Bureau of Standards survey.[10] The melting point (actually the triple point) is that measured by Giaque and Overstreet.[11] The heat of vaporization at the boiling point is that of Osborne and Van Dusen.[12]

The vapor pressures of ammonia at T_1, T_2, T_3, and T_4 were calculated from the equation of Cragoe et al.[10]:

$$\log P_{atm} = 27{\cdot}376004 - 1914{\cdot}9569/T - 8{\cdot}4598324 \log T + 2{\cdot}39309 \times 10^{-3} T + 2{\cdot}955214 \times 10^{-6} T^2 \qquad (4)$$

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[*] Tables 3 through 22 are grouped together in the final section of this report.

The corresponding specific volumes of saturated liquid ammonia were calculated from the equation of Cragoe and Harper:[13]

$$v_\ell = \frac{4\cdot2830 + 0\cdot813055\ (133-t)^{1/2} - 0\cdot0082861(133-t)}{1 + 0\cdot424805\ (133-t)^{1/2} + 0\cdot015938(133-t)} \qquad (5)$$

where v_ℓ is in $cm^3\ g^{-1}$ and t is in degrees centigrade. Note that this equation, as given by Davies, should have a plus sign in front of the last term in the denominator. The corresponding specific volumes of saturated liquid ammonia were calculated from the equation of Cragoe and co-workers:[14]

$$\log v_g = 300\left[\frac{6.46344}{T} - 0\cdot106887 + 0\cdot0356803 \log T\right] + 0\cdot0862366\ (406\cdot1 - T)^{1/2} + 0\cdot002667(406\cdot1 - T) \qquad (6)$$

where v_g is in $cm^3\ g^{-1}$ and T is in kelvin. The specific heats of saturated liquid ammonia were calculated by the equation of Osborne and Van Dusen:[15]

$$c_\sigma = 3\cdot1365 - 0\cdot00057t + \frac{16\cdot842}{(133-t)^{\frac{1}{2}}} \qquad (7)$$

where c_σ is in $Jg^{-1}\ K^{-1}$ and t is in degrees centigrade. The heat capacity of the ideal gas (at P = 0) was calculated from the experimental equation of Osborne and co-workers:[16]

$$c_p^\circ = 1\cdot1255 + 0\cdot00238T + 76\cdot8/T \qquad (8)$$

where c_p° is in $Jg^{-1}\ K^{-1}$ and T is in kelvin.

Methylamine. The critical temperature and critical pressure of methylamine, shown in Table 4, were determined by Berthoud.[17] A critical volume of 140 $cm^3\ mol^{-1}$ was listed by Reid et al.;[18] however, the original reference was not given. The original reference for Gallant's[19] cited value of 144 $cm^3\ mol^{-1}$ was also unobtainable. Given that the value of v_c estimated by Vetere's method[20] is 130 $cm^3\ mol^{-1}$, it appears that there is no reliable literature value for v_c.

The melting point, boiling point, and heat of vaporization of methylamine were determined by Aston et al.[21] The vapor pressures of pure methylamine were determined by Aston et al. at T_3 and T_4. The self-consistency of Aston's data was shown by comparison of the experimental heat of vaporization with that calculated from the vapor pressure curve at the boiling point: the two values differed by only 0.4%. The vapor pressure at T_1 was determined by Berthoud.[17] The vapor pressure at 298.15 K was calculated to be 3.53 atm from the Antoine equation given by Reid et al.[18] However, because the vapor pressure calculated from this equation deviates by ±0.6% from the value of Aston at 267.2 K and by ±1.3% for the value of Berthoud at 314.2 K, the interpolated value at 298.15 K is not considered reliable to ±1.0%.

The specific volumes of saturated liquid methylamine at T_2, T_3 and T_4 were calculated from the equation of Felsing and Thomas,[22]

$$D(\text{g cm}^{-3}) = 0.93249 - 6.09221 \times 10^{-4}\ T - 106.443 \times 10^{-8}\ T^2 \qquad (9)$$

This equation was based on data covering the range of -83°C to 20°C. Because of the low temperature dependence of the liquid density, extrapolation of the data to T_2 (30°C) was considered to be reliable.

The heat capacity of methylamine at constant pressure was determined by Aston[21] from 14.8 K to 259.3 K. The measured value actually appears to be that of c_σ, the heat capacity of the saturated liquid. However, because the difference between c_p and c_σ at temperatures below the boiling point is negligible, this distinction is not important.

The ideal heat capacities of methylamine vapor were calculated by the reporters from the spectroscopic data of Owens and Barker[23] at T_1, T_2, T_3, and T_4. These spectroscopic data are the same as those used by Aston and Doty[24] and by Kobe and Harrison[25] to calculate $c°_p$ for methylamine at other temperatures.

The specific volumes of the saturated vapor at T_3 (P = 0.587 atm at 255.60 K) and T_4 (P = 0.04572 atm at 214.265 K) were calculated from equations (31) and (32) and the Lee-Kesler tables,[26] as described in the subsection on estimation methods.

Ethylamine. The critical temperature and critical pressure of ethylamine, shown in Table 5, are those determined by Berthoud.[17] The critical volume of ethylamine was determined by Pohland and Mehl.[27] The critical temperature determined by Pohland and Mehl was 0.2 K higher than that of Berthoud. The melting point, boiling point, and vapor pressure were also measured by Pohland and Mehl.[27] Their vapor pressure data from 211.9 K to 297.0 K were fitted to:

$$\log P = 21.5535 - \frac{2093.686}{T} - 4.61703 \log T - 2.74 \times 10^{-4}\ T \quad (10)$$

The heat of vaporization was calculated from this equation together with the measured specific volumes of the vapor and liquid. This value is 0.6% higher than the value given by the Matheson Gas Data Book[28] and 1.9% higher than the value estimated by the Chen Method.[26] The vapor pressures at T_1 and T_2 are those measured by Berthoud.[17] Where the data overlap at 288.6 K, the calculated value of equation (10) is within 0.4% of the value measured by Berthoud.

The specific volumes of the saturated liquid at T_2, T_3, and T_4 were measured by Pohland and Mehl,[27] whereas the specific volumes of the saturated vapor at T_3 and T_4 were calculated from equations (31) and (32) using the vapor pressure data of Pohland and Mehl. The specific volumes of the saturated vapor at T_1 and T_2 were interpolated from measured values of Pohland and Mehl, and will be confirmed by our own measurements.

The specific heats of the saturated liquid and low pressure vapor of ethylamine have been estimated in the literature,[29] but the values are clearly not reliable to 1%.

Chlorodifluoromethane (R-22). The critical properties of R-22 listed in Table 6 are those selected by Kudchadker et al.[2] in their review of the critical constants of organic substances. The critical temperature and critical volume are those measured by Benning and McHarness,[30] and the critical pressure is that measured by Du Pont.[31]

The pressure value differs from that of Benning and McHarness by 0.8%.

The normal boiling point, freezing point, and enthalpy of vaporization were measured by Neilson and White.[32]

The vapor pressures of R-22 at T_1, T_2, T_3, and T_4 are given by the equation of Martin,[31]

$$\log P = A - \frac{B}{T} - C \log T + DT + \frac{E\ (F-T)}{FT} \log\ (F-T) \tag{11}$$

where A = 29.35754453, B = 3845.193152, C = 7.86103122, D = 0.002190939044, E = 305.8268131, and F = 686.1. For equation (11), the range of data is 0.08 psia to 692 psia, and the average deviation is 0.11%. Also, P is in psia and T is in degrees Rankine, which is based on the data of Michels[31] and the Du Pont Company.[31] Over the range T_1 to T_3, these data are within 1% of the data of Benning and McHarness.[33]

The specific volumes of the saturated liquid were calculated from the equation given by Du Pont.[31]

$$d_f = A + B\left(1-\frac{T}{Tc}\right)^{1/3} + C\left(1-\frac{T}{Tc}\right)^{2/3} \tag{12}$$

$$+ D\left(1-\frac{T}{Tc}\right) + E\left(1-\frac{T}{Tc}\right)^{4/3}$$

where A = 32.76, B = 54.6344093, C = 36.74892, D = 22.2925657, and E = 20.47328862. For equation (12), the range of data is 100 lb ft^{-3} to 51 lb ft^{-3}, and the average deviation is 0.08%. Also, d_f (lb ft^{-3}) is the density, and T and T_c are in degrees Rankine. This equation appears to be based on the experimental values of Benning and McHarness;[30] the calculated values deviate from these experimental values by less than 0.2% over the range T_1 to T_4. The specific volumes of the saturated vapor were measured by Michels and confirmed by data from the Du Pont Company.[31]

The specific heat of the saturated liquid was measured by Benning et al.[34] from 256 K to 328 K and by Neilson and White[32] from 122 K to 226 K. The specific heat of the vapor at T_1, T_2, T_3, and T_4 was calculated from the equation of Du Pont,[31] which is based on spectroscopic data:

$$c_v^\circ = a + \frac{b}{T^2} + cT + dT^2 \qquad (13)$$

where $a = 2.812836 \times 10^{-2}$, $b = 257.341$, $c = 2.255408 \times 10^{-4}$ and $d = -6.509607 \times 10^{-8}$, and where c_v° is in cal g^{-1} K^{-1} and T is in degrees Rankine. To convert these values to c_p°, as shown in Table 6, the following equation was used

$$c_p^\circ = c_v^\circ + R \qquad (14)$$

where R is the gas constant. Adding Berthelot's[35] correction for gas nonideality, the calculated c_p value at 1 atm pressure is approximately 3% higher than that measured calorimetrically by Benning et al.[34] at T_1.

Fluorodichloromethane (R-21). All the data listed in Table 7 for R-21, with the exception of c_p° values, were measured or calculated from the data of Benning, McHarness, and co-workers.[36]

The vapor pressures of R-21 over the range from -30°C to 175°C were fitted to the following equation by Benning and McHarness:[33]

$$P = (0.0003593T - 0.2038)\, d^3 + (0.004642T - 7.316)\, d^2 + 0.10427\, Td \qquad (15)$$

where d is the density in lb ft^{-3}, P is in psia, and T is in degrees Rankine.

The heat capacity of saturated R-21 was measured by Benning et al.[34] from -12°C to 65°C and fitted to the following equation:

$$c_\sigma = 0.2471 + 0.000189\ t \qquad (16)$$

where c_σ is in cal g^{-1} K^{-1} and t is in degrees centigrade. Because of the small temperature dependence of c_σ, extrapolation of the data to T_4 (t = -40°C) is considered to be reliable.

Absorbents

Ethylene glycol. The critical properties of ethylene glycol have not been measured,[37] probably because of the documented[38] thermal decomposition of ethylene glycol at temperatures slightly higher than the normal boiling point.

There is some uncertainty in the freezing point, because of supercooling, and in the boiling point, because of thermal decomposition of ethylene glycol. The values listed in Table 8 are those selected by Jones and Tamplin[39] in their review of the physical properties of ethylene glycol. The heat of vaporization at the boiling point has been measured calorimetrically and from the vapor pressure curve. However, because the calorimetric measurement was performed in 1898[40] and because of the reported difficulties[38] with thermal decomposition of ethylene glycol around the boiling point, these reported values are not considered reliable.

The vapor pressure of ethylene glycol has been reported by several investigators. Jones and Tamplin[39] compiled the data from all known sources in 1951 and, after plotting the data and discarding obviously bad values, fitted the vapor pressures to the Antoine equation

$$\log P = a + \frac{b}{c + t} \tag{17}$$

where a = 7.8808, b = -1957, and c = 193.8, and where t is in degrees centigrade and P is in torr. In Table 8, T_2 through T_4 were calculated from an estimated T_c = 645 K. The vapor pressure at T_1 is not given because Equation (17) is valid only in the range of ∿0.5-1500 torr. Because of possible thermal decomposition of ethylene glycol at T_1, it is not certain if the vapor pressure can be reliably measured at T_1.

The specific volume of saturated ethylene glycol vapor has not been directly measured. The calculation of v_g from the vapor pressures below atmospheric pressure is considered too unreliable because the uncertainty in the vapor pressure measurements is only slight less than ±1% and the uncertainty in the compressibility factor, Z, may be as high as ±0.5% for a polar molecule such as ethylene glycol.

The specific volumes of saturated ethylene glycol liquid listed in Table 8 were measured over the temperature range T_1 through T_4 by Costello and Bowden.[41] These data are within 0.3% of the values calculated from the earlier equation given by Gibson and Loeffler:[42]

$$v_\ell = 0.924848 + 6.29796 \times 10^{-4}\ (t-65) + 9.2444 \times 10^{-7}\ (t-65)^2 + 3.057 \times 10^{-9}\ (t-65)^3 \qquad (18)$$

where v_ℓ is in $cm^3\ g^{-1}$ and t is in degrees centigrade.

The saturated liquid specific heats of ethylene glycol over the temperature range of 0°C to 220°C were recently measured by Stephens and Tamplin[5] using a Perkin-Elmer differential scanning calorimeter. Reproducibility of the results was well within ±1%. Furthermore, these results were within 2% of the values calculated from the equation of Jones and Tamplin.[39]

$$C = 0.538 + 0.00113\ t \qquad (19)$$

where C is in cal $g^{-1}\ K^{-1}$ and t is in degrees centigrade.

1,4-Butanediol. Very little data have been reported on 1,4-butanediol. The melting point and boiling point listed in Table 9 are those given by Du Pont.[43] The vapor pressure at 127°C is given as 20 torr by Livengood.[44] The specific volume of the saturated liquid at 25°C is given as 88.79 $cm^3\ mol^{-1}$ by Du Pont.

Diethylene glycol dimethyl ether (DGDE). The only data obtained for DGDE were vapor pressures measured from 20°C to 60°C and liquid densities measured from 25°C to 115°C by Gallaugher and Hibbert.[38] According to these workers, DGDE begins to decompose thermally at 60°C; therefore, their determination of the boiling point at 159.8°C may not be reliable. The equation they give for the vapor pressure at DGDE is:

$$\log P = 2251.5/T + 8.0837 \qquad (20)$$

where P is in torr and T is in kelvin. The equation they give for the liquid density is

$$d = -0.00106\ t + 0.9829 \qquad (21)$$

where d is in g cm^{-3} and t is in degrees centigrade.

N,N-Dimethylacetamide (DMA). The boiling point and melting point of DMA are those reported by Du Pont.[45] Estimated critical properties of DMA have also been reported by Du Pont.[46]

The measurement of the critical properties may be unreliable if DMA thermally decomposes above 350°C, as reported by Du Pont.[46] The heat of vaporization listed in Table 11 was reported by Du Pont,[45] but no description was given of the experimental method used.

The vapor pressures of DMA are reported by Du Pont[46] in graphical form from 20°C to 380°C, but again the experimental method and data points are not given. The vapor pressures have been determined from 30°C to 90°C by Gopal and Rizvi[47] and presented in graphical form from 40°C to 240°C by Gallant.[48] However, these data deviate by more than 1% from those given by Du Pont, so that none of the data are considered reliable.

The liquid density of DMA is reported by Du Pont[46] in graphical form from -10°C to 170°C, but the experimental method and data points are not given. The specific heat of DMA at 20°C and 80°C is also given by Du Pont[46] without experimental details.

N,N-Dimethylhexanamide (DMH) and N,N-Dimethyldecanamide (DMD). No reliable data were found for DMH or DMD.

Fluid Mixture Data

No reliable literature data were found for any of the mixtures listed in Table 2.

Estimation Methods

Estimation methods recommended by Reid, Prausnitz, and Sherwood[49] have enabled us to estimate unmeasured data and thereby refine our experimental protocols. These methods are described below.

Lydersen's method[20] uses structural contributions to estimate T_c, P_c, and v_c:

$$\begin{aligned} T_c &= T_b\left[0.567 + \Sigma\Delta_T - (\Sigma\Delta_T)^2\right]^{-1} \\ P_c &= M(0.34 + \Sigma\nabla_p)^{-2} \\ v_c &= 40 + \Sigma\nabla_v \end{aligned} \tag{22}$$

The normal boiling point, T_b, and molecular weight, M, together with the Δ increments (obtained from Table 2-1 of Reid, Prausnitz, and Sherwood)[49] were used to calculate the critical properties of the pure fluids. The typical errors in estimating T_c are usually less than 2% for nonpolar low-molecular-weight materials. The typical errors, however, increase by up to 5% for high-molecular-weight fluids ($M > 100$) and may be higher for molecules with multifunctional polar groups, such as ethylene glycol or 1,4-butanediol. The corresponding errors for P_c and v_c are roughly double the values for T_c. Vetere's method, another group contribution method for estimating v_c, is generally more accurate than Lydersen's method. Vetere's equation[20] is

$$v_c = 33.04 + \left[\sum_i (\Delta V_i M_i)\right]^{1.029} \tag{23}$$

where V_i is given in Table 2-4 of Reid et al.[20] for most groups and M_i is the molecular weight of the group.

Comparisons of experimental and estimated critical properties for the pure refrigerants and absorbents are given in Tables 14, 15, and 16.

The vapor pressures and specific volumes of the saturated liquids and saturated vapors of the pure fluids were estimated from reduced properties using corresponding states theories. These calculations required knowledge of T_c, P_c, and v_c to calculate the reduced temperature ($T_r = T/T_c$), reduced pressure ($P_r = P/P_c$), and reduced volume ($v_r = v/v_c$), and a means of estimating the acentricity factor (ω). The acentricity factor is a measure of the nonsphericity of the fluid molecule and is defined by[2]

$$\omega = -\log P_r(\text{at } T_r = 0.7) - 1.00 \tag{24}$$

If the vapor pressure at $T_r = 0.7$ is not known, ω can be estimated using the Lee-Kesler correlation method.[26]

The Pitzer expansion is[26]

$$\ell n\ P \quad = f^{(0)}(T\ ) + f^{(1)}(T\ ) \tag{25}$$

where P_r and T_r are the reduced pressure and reduced temperature, respectively, and ω is the acentric factor, was used to estimate pure fluid vapor pressures. The functions $f^{(0)}$ and $f^{(1)}$ were calculated using the analytical equations of Lee and Kesler:

$$f^{(0)} = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \ln T_r + 0.169347T_r^6$$

$$f^{(1)} = 15.2518 - \frac{15.6875}{T_r} - 13.472 \ln T_r + 0.43577T_r^6 \qquad (26)$$

The acentric factor ω was calculated by substituting the reduced temperature and reduced pressure at the normal boiling point into Equations (25) and (26) and rearranging to give

$$\omega = \frac{-\ln P_c - f^{(0)}(\theta)}{f^{(1)}(\theta)} \qquad (27)$$

where $\theta = T_b/T_c$.

Table 17 indicates that vapor pressures estimated using the Lee-Kesler method[26] are most accurate for R-21 and R-22 and generally are closer to experimental values at higher reduced temperatures. Because the estimation of ω is sensitive to the ratio T_b/T_c, where T_b is the normal boiling temperature, and because T_c was estimated for all of the absorbents, it is expected that ω (and hence the estimated vapor pressures of the absorbents) may deviate significantly (by perhaps an order of magnitude) from experimental values. Nevertheless, these estimated values are still useful for determining the type and sensitivity of pressure measurements required to perform the designated work.

The Gunn-Yamada method[50] was used to estimate the specific volumes of the saturated liquids (v_ℓ):

$$\frac{v_\ell}{v^r} = \frac{v_r^{(0)}(T_r)[1 - \omega\Gamma(T_r)]}{v_r^{(0)}(T_r^R)[1 - \omega\Gamma(T_r^R)]} \qquad (28)$$

where v^R is the specific volume of the saturated liquid at a reference temperature, T^R, and

$$v_r^{(0)} = (0.33593 - 0.33953T_r + 1.51941T_r^2 - 2.02512T_r^3 + 1.11422T_r^4 \qquad (29)$$

$$\Gamma = 0.29607 - 0.09045T_r - 0.04842T_r^2 \qquad (30)$$

These estimated values are seen in Table 18 to approximate reliable experimental values. Because of their insensitivity to ω, it is expected that the estimated values of v_ℓ for the absorbents are also close to experimental values. In fact, once accurate ω values for the absorbents are known, the Gunn-Yamada estimation method will provide a good check on the accuracy of our experimental data.

Specific volumes of the saturated vapors of the pure fluids were estimated (see Table 19) using the Lee-Kesler tables[50] to calculate the compressibility factor Z:

$$Z = Z^{(0)}(T_r,P_r) + \omega\, Z^{(1)}(T_r,P_r) \tag{31}$$

and hence the vapor density:

$$v_g = \frac{ZRT}{P} \tag{32}$$

where R is the gas constant. If the vapor pressure is accurately known, then v_g can be very accurately estimated, particularly at low pressure where the fluid acts like an ideal gas with Z approximately equal to one. The accuracy of this estimation method can be seen in the very small deviations between estimated and experimental v_g values for the pure refrigerants.

The heat capacities of the ideal gases (c_p°) in Table 20 were estimated by the group additivity method of Benson et al.[51] The heat capacity of the saturated liquid was calculated (see Table 21) using the Yuan and Stiel equation[51]

$$c_\sigma - c_p^\circ = (\Delta c_\sigma)^\circ + \omega\, (\Delta c_\sigma)^{(1)} \tag{33}$$

where (Δc_σ) and $(\Delta c_\sigma)^{(1)}$ are functions of T_r. The heat of vaporization at the normal boiling point was estimated[51] (Table 22) by the equation of Chen:

$$\Delta H_v = R\, T_b\, \frac{3.978\,\theta - 3.938 + 1.555\, \ell n\, P_c}{1.07 - \theta} \tag{34}$$

where $\theta = T_b/T_c$. The estimated ideal heat capacities of the gases and the heats of vaporization should be accurate to within 5-10% for the absorbents. The minima in the estimated heat capacities of saturated liquid ethylene glycol and 1,4-butanediol between $T_r = 0.5$ and $T_r = 0.7$ is probably a result of using calculated ω values that are far too high.

TABLES OF EXPERIMENTAL DATA

Table 3

THERMODYNAMIC DATA FOR AMMONIA

		Literature		Ref.	This Work
T_m (K)		195.41		11	
T_b (K)		239.76		10	
T_c (K)		405.6		9	
P_c (atm)		115.5		9	
V_c (cm^3 mol^{-1})		72.47		9	
ΔH_v (kcal mol^{-1})		5.5827		12	
P (atm)	@ T_1	34.14	@ 345	10	
	T_2	5.446	@ 280	10	
	T_3	1.0124	@ 240	10	
	T_4	0.08553	@ 200	10	
v_ℓ (cm^3 mol^{-1})	@ T_1	32.53	@ 345	13	
	T_2	27.07	@ 280	13	
	T_3	24.99	@ 240	13	
	T_4	23.37	@ 200	13	
v_g (cm^3 mol^{-1})	@ T_1	613.2	@ 345	14	
	T_2	3,882	@ 280	14	
	T_3	18,905	@ 240	14	
	T_4	189,730	@ 200	14	
c_σ (cal mol^{-1} k^{-1})	@ T_1	21.37	@ 345	15	
	T_2	18.85	@ 280	15	
	T_3	18.15	@ 240	15	
	T_4	17.58	@ 200	15	
c_p° (cal mol^{-1} k^{-1})	@ T_1	8.830	@ 345	16	
	T_2	8.411	@ 280	16	
	T_3	8.209	@ 240	16	
	T_4	8.082	@ 200	16	

Table 4

THERMODYNAMIC DATA FOR METHYLAMINE

		Literature	Ref.	This Work
T_m (K)		179.69	21	
T_b (K)		266.83	21	
T_c (K)		430.1	17	
P_c (atm)		73.6	17	
V_c (cm^3 mol^{-1})				
ΔH_v (kcal mol^{-1})		6.169 ± 0.03	21	
P (atm)	@ T_1	33.32 @ 385.55	17	
	T_2			
	T_3	0.5870 @ 255.598	21	
	T_4	0.04572 @ 214.265	21	
v_ℓ (cm^3 mol^{-1})	@ T_1			
	T_2	47.78 @ 303.15	22	
	T_3	44.10 @ 258.15	22	
	T_4	41.18 @ 213.15	22	
v_g (cm^3 mol^{-1})	@ T_1			
	T_2			
	T_3	35,140. @ 255.6		
	T_4	383,640. @ 214.265		
c_σ (cal mol^{-1} k^{-1})	@ T_1			
	T_2			
	T_3	24.33 @ 259.28	21	
	T_4	24.07 @ 212.46	21	
c_p^o (cal mol^{-1} k^{-1})	@ T_1	13.70 @ 365.	23	
	T_2	12.19 @ 300.	23	
	T_3	11.34 @ 260.	23	
	T_4	10.53 @ 215.	23	

Table 5

THERMODYNAMIC DATA FOR ETHYLAMINE

		Literature		Ref.	This Work
T_m (K)		192.15		27	
T_b (K)		289.65		27	
T_c (K)		456.35		17	
P_c (atm)		55.54		17	
v_c (cm^3 mol^{-1})		185.2		27	
ΔH_v (kcal mol^{-1})		6.53		27	
P (atm)	@ T_1	15.34	@ 383.35	17	
	T_2	2.75	@ 319.15	17	
	T_3	0.4926	@ 273.42	27	
	T_4	0.03461	@ 227.92	27	
v_ℓ (cm^3 mol^{-1})	@ T_1				
	T_2	69.05	@ 319.15	27	
	T_3	63.89	@ 273.15	27	
	T_4	59.24	@ 223.65	27	
v_g (cm^3 mol^{-1})	@ T_1	1,682	@ 383.15*	27	
	T_2	9,108	@ 319.15*	27	
	T_3	45,211	@ 273.81+	27	
	T_4	539,253	@ 228.18+	27	
c_σ (cal mol^{-1} k^{-1})	@ T_1				
	T_2				
	T_3				
	T_4				
c°_p (cal mol^{-1} k^{-1})	@ T_1				
	T_2				
	T_3				
	T_4				

*Interpolated data

+Calculated from equations 31 and 32.

Table 6

THERMODYNAMIC DATA FOR CHLORODIFLUOROMETHANE (R-22)

		Literature		Ref.	This Work
T_m (K)		115.73		32	
T_b (K)		232.5		32	
T_c (K)		369.2		30	
P_c (atm)		49.1		31	
V_c (cm^3 mol^{-1})		165		30	
ΔH_v (kcal mol^{-1})		4.8325		32	
P (atm)	@ T_1	15.13	@ 313.15	31	
	T_2	3.028	@ 259.15	31	
	T_3	0.635	@ 223.15	31	
	T_4	0.04835	@ 183.15	31	
v_ℓ (cm^3 mol^{-1})	@ T_1	76.44	@ 313.15	31	
	T_2	64.83	@ 259.15	31	
	T_3	60.12	@ 223.15	31	
	T_4	55.96	@ 183.15	31	
v_g (cm^3 mol^{-1})	@ T_1	1,308.8	@ 313.15	31	
	T_2	6,712.5	@ 259.15	31	
	T_3	28,066	@ 223.15	31	
	T_4	309,638	@ 183.15	31	
c_σ (cal mol^{-1} k^{-1})	@ T_1	27.1	@ 313.15	34	
	T_2	23.40	@ 255.85	34	
	T_3	22.191	@ 220.04	32	
	T_4	22.050	@ 188.5	32	
c_p° (cal mol^{-1} k^{-1})	@ T_1	13.70	@ 313.15	31	
	T_2	12.37	@ 259.15	31	
	T_3	11.49	@ 223.15	31	
	T_4	10.45	@ 183.15	31	

Table 7

THERMODYNAMIC DATA FOR DICHLOROFLUOROMETHANE (R-21)

		Literature		Ref.	This Work
T_m (K)		138.2		36	
T_b (K)		282.05		36	
T_c (K)		451.65		30	
P_c (atm)		51.0		30	
V_c (cm^3 mol^{-1})		197.2		36	
ΔH_v (kcal mol^{-1})					
P (atm)	@ T_1	16.4	@ 384.15	33	
	T_2	3.10	@ 315.15	33	
	T_3	0.615	@ 270.15	33	
	T_4	0.0556	@ 225.15	33	
v_ℓ (cm^3 mol^{-1})	@ T_1	90.57	@ 384.15	36	
	T_2	77.76	@ 315.15	36	
	T_3	71.85	@ 270.15	36	
	T_4	67.70*	@ 230.15	36	
v_g (cm^3 mol^{-1})	@ T_1	1460	@ 384.15	36	
	T_2	7800	@ 315.15	36	
	T_3	35,410	@ 270.15	36	
	T_4				
c_σ (cal mol^{-1} k^{-1})	@ T_1	27.5*	@ 380.15	34	
	T_2	26.2	@ 313.15	34	
	T_3	25.4	@ 273.15	34	
	T_4	24.6*	@ 230.15	34	
c_p° (cal mol^{-1} k^{-1})	@ T_1				
	T_2				
	T_3				
	T_4				

*extrapolated

Table 8

THERMODYNAMIC DATA FOR ETHYLENE GLYCOL

		Literature		Ref.	This Work
T_m (K)		260.15		39	
T_b (K)		470.8		39	
T_c (K)					
P_c (atm)					
V_c (cm^3 mol^{-1})					
ΔH_v (kcal mol^{-1})					
P (atm)	@ T_1				
	T_2	0.582	@ 453.15	39	
	T_3	0.0438	@ 387.15	39	
	T_4	0.000940	@ 323.15	39	
v_ℓ (cm^3 mol^{-1})	@ T_1	69.8	@ 553.15	41	
	T_2	62.75	@ 453.15	41	
	T_3	59.62	@ 393.15	41	
	T_4	56.79	@ 323.15	41	
v_g (cm^3 mol^{-1})	@ T_1				
	T_2				
	T_3				
	T_4				
c_σ (cal mol^{-1} k^{-1})	@ T_1				
	T_2	46.7	@ 453.15 K	5	
	T_3	42.7	@ 393.15 K	5	
	T_4	37.55	@ 323.15 K	5	
c_p° (cal mol^{-1} k^{-1})	@ T_1				
	T_2				
	T_3				
	T_4				

Table 9

THERMODYNAMIC DATA FOR 1,4-BUTANEDIOL

		Literature	Ref.	This Work
T_m (K)		293.15	43	
T_b (K)		228	43	
T_c (K)				
P_c (atm)				
v_c (cm^3 mol^{-1})				
ΔH_v (kcal mol^{-1})				
P (atm)	@ T_1			
	T_2			
	T_3			
	T_4			
v_ℓ (cm^3 mol^{-1})	@ T_1			
	T_2			
	T_3			
	T_4			
v_g (cm^3 mol^{-1})	@ T_1			
	T_2			
	T_3			
	T_4			
c_σ (cal mol^{-1} k^{-1})	@ T_1			
	T_2			
	T_3			
	T_4			
c_p° (cal mol^{-1} k^{-1})	@ T_1			
	T_2			
	T_3			
	T_4			

Table 10

THERMODYNAMIC DATA FOR DIETHYLENE CLYCOL DIMETHYL ETHER

		Literature	Ref.	This Work
T_m (K)				
T_b (K)				
T_c (K)				
P_c (atm)				
V_c (cm^3 mol^{-1})				
ΔH_v (kcal mol^{-1})				
P (atm)	@ T_1			
	T_2			
	T_3			
	T_4			
v_ℓ (cm^3 mol^{-1})	@ T_1			
	T_2			
	T_3			
	T_4			
v_g (cm^3 mol^{-1})	@ T_1			
	T_2			
	T_3			
	T_4			
c_σ (cal mol^{-1} k^{-1})	@ T_1			
	T_2			
	T_3			
	T_4			
c_p° (cal mol^{-1} k^{-1})	@ T_1			
	T_2			
	T_3			
	T_4			

Table 11

THERMODYNAMIC DATA FOR N,N-DIMETHYLACETAMIDE

		Literature	Ref.	This Work
T_m (K)		253.2	45	
T_b (K)		439.3	45	
T_c (K)				
P_c (atm)				
V_c ($cm^3\ mol^{-1}$)				
ΔH_v ($kcal\ mol^{-1}$)		10.36	45	
P (atm)	@ T_1			
	T_2			
	T_3			
	T_4			
v_ℓ ($cm^3\ mol^{-1}$)	@ T_1			
	T_2			
	T_3			
	T_4			
v_g ($cm^3\ mol^{-1}$)	@ T_1			
	T_2			
	T_3			
	T_4			
c_σ ($cal\ mol^{-1}\ k^{-1}$)	@ T_1			
	T_2			
	T_3			
	T_4			
c_p° ($cal\ mol^{-1}\ k^{-1}$)	@ T_1			
	T_2			
	T_3			
	T_4			

Table 12

THERMODYNAMIC DATA FOR N,N-DIMETHYLHEXANAMIDE

		Literature	Ref.	This Work
T_m (K)				
T_b (K)				
T_c (K)				
P_c (atm)				
V_c (cm^3 mol^{-1})				
ΔH_v (kcal mol^{-1})				
P (atm)	@ T_1			
	T_2			
	T_3			
	T_4			
v_ℓ (cm^3 mol^{-1})	@ T_1			
	T_2			
	T_3			
	T_4			
v_g (cm^3 mol^{-1})	@ T_1			
	T_2			
	T_3			
	T_4			
c_σ (cal mol^{-1} k^{-1})	@ T_1			
	T_2			
	T_3			
	T_4			
c_p° (cal mol^{-1} k^{-1})	@ T_1			
	T_2			
	T_3			
	T_4			

Table 13

THERMODYNAMIC DATA FOR N,N-DIMETHYLDECANAMIDE

		Literature	Ref.	This Work
T_m (K)				
T_b (K)				
T_c (K)				
P_c (atm)				
V_c ($cm^3\ mol^{-1}$)				
ΔH_v ($kcal\ mol^{-1}$)				
P (atm)	@ T_1			
	T_2			
	T_3			
	T_4			
v_ℓ ($cm^3\ mol^{-1}$)	@ T_1			
	T_2			
	T_3			
	T_4			
v_g ($cm^3\ mol^{-1}$)	@ T_1			
	T_2			
	T_3			
	T_4			
c_σ ($cal\ mol^{-1}\ k^{-1}$)	@ T_1			
	T_2			
	T_3			
	T_4			
c_p° ($cal\ mol^{-1}\ k^{-1}$)	@ T_1			
	T_2			
	T_3			
	T_4			

Table 14

ESTIMATED CRITICAL TEMPERATURES (T_c, K) USING LYDERSEN'S METHOD[2]

	Experimental	Estimated	Percent Difference
Ammonia	405.6	402	-0.9
Methylamine	430	434	
Ethylamine	456	458	0.4
R-22	369.2	370.4	0.3
R-21	451.7	449.9	0.4
Ethylene glycol	NA	645	
1,4-Butanediol	NA	670	
DGDE	NA	607	
DMA	NA	657	
DMH	NA	680	
DMD	NA	718	
			Avg 0.6

Table 15

ESTIMATED CRITICAL PRESSURES (P_c, atm) USING LYDERSEN'S METHOD[2]

	Experimental	Estimated	Percent Difference
Ammonia	111.5	90	-19.3
Methylamine	73.6	70.9	-3.7
Ethylamine	55.5	57.1	2.9
R-22	49.1	49.8	1.4
R-21	51.0	51.1	1.0
Ethylene glycol	NA	74.3	
1,4-Butanediol	NA	48.2	
DGDE	NA	28.2	
DMA	NA	39.7	
DHM	NA	25.1	
DMD	NA	18.3	
			Avg 5.7

Table 16

ESTIMATED CRITICAL VOLUMES (v_c, $cm^3\ mol^{-1}$), USING VETERE'S METHOD[2]

	Experimental	Estimated	Percent difference
Ammonia	72.47	71.9	0.8
Methylamine	140	130	7.1
Ethylamine	185.3	185.8	0.3
R-22	165	167	1.2
R-21	197.2	201.8	2.3
Ethylene glycol	NA	169	
1,4-Butanediol	NA	281	
DGDE	NA	437	
DMA	NA	298	
DMH	NA	527	
DMD	NA	759	
			Avg 2.3

Table 17

VAPOR PRESSURES (P, atm) ESTIMATED USING LEE-KESLER METHOD[3]

	0.5	0.6	0.7	0.85
Ammonia	0.113 (6.5)	1.30 (8.3)	6.8 (9.7)	35.8 (5.3)
Methylamine	0.056 (12.0)	0.71 (4.8)	4.1 (11.2)	22.8 (1.6)
Ethylamine	0.045 (-11.8)	0.57 (13.3)	3.1 (7.7)	17.3 (3.0)
R-22	0.061 (12.5)	0.645 (10.3)	3.2 (-14.3)	16.2 (5.3)
R-21	0.061 (5.2)	.657 (3.0)	3.29 (3.1)	16.7 (1.8)
Ethylene glycol	1.6×10^{-4}	0.045	0.56	11.0
1,4-Butanediol	1.4×10^{-6}	0.0033	0.083	4.2
DGDE	0.041	0.14	0.88	7.1
DMA	0.020	0.37	1.9	11.7
DMH	0.0039	0.13	0.81	6.4
DMD	8.0×10^{-4}	0.05	0.38	4.0
	Avg (9.6)	(7.9)	(9.2)	(3.4)

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[*] Numbers in parentheses are percent difference between estimated and experimental values.

Table 18

ESTIMATED SPECIFIC VOLUMES OF SATURATED LIQUIDS (v_ℓ, $cm^3 \cdot mol^{-1}$) USING THE GUNN-YAMADA METHOD[4]

	T_r			
	0.5	0.6	0.7	0.85
Ammonia	23.5 (0.5)	25.1 (0.6)	27.2 (0.4)	31.8 (-2.2)
Methylamine	41.1 (-0.2)	44,0 (-0.63)	47.6 (-0.4)	55.7
Ethylamine	59.7 (0.8)	64.0 (0.1)	69.2 (0.2)	81.0
R-22	56.0 (0.1)	59.9 (-0.3)	64.8 (-0.1)	75.7 (-10)
Ethylene glycol	56.9	62.0	68.3	82.3
1,4-Butanediol	94.4	105	118	147
DGDE	141	152	165	194
DMA	96.5	103	112	131
DMH*				
DMD*				

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*Reference volume not available to make estimation

Table 19

ESTIMATED SPECIFIC VOLUMES OF THE SATURATED VAPORS (v_g, $cm^3 \cdot mol^{-1}$) USING THE LEE-KESLER METHOD[4]

	T_r			
	0.5	0.6	0.7	0.85
Ammonia	191,310 (0.8)	19,090 (1.0)	4090 (5.4)	641 (4.5)
Methylamine	383,640	35,140	6840	578
Ethylamine	539,250	45,210	9225	1632
R-22	309,660 (0.006)	28,110 (0.16)	6760 (0.7)	1364 (4.2)
Ethylene glycol	2.0×10^8	704,000	65,200	3500
1,4-Butanediol	1.5×10^{10}	1×10^7	462,000	10,080
DGDE	8.9×10^6	209,000	37,800	72.3
DMA	1.9×10^6	85,200	18,600	3140
DMH	1.1×10^7	252,000	48,200	5930
DMD	6.4×10^7	701,000	104,800	10,200

Table 20

IDEAL HEAT CAPACITIES (c_p^o, cal mol^{-1}) OF GASES ESTIMATED USING BENSON'S METHOD[5]

	T_r			
	0.5	0.6	0.7	0.85
Methylamine			11.91 (-23)	13.5 (-1.5)
Ethylamine			18.0	20.8
Ethylene glycol	19.55	22.3	24.5	27.7
1,4-Butanediol	32.0	26.6	40.8	46.4
DGDE	43.0	50.0	56.4	64.3
DMA	29.4	33.8	38.1	43.8
DMH	54.3	63.0	71.0	81.2
DMD	82.3	95.0	107.2	122.0

Table 21

ESTIMATED HEAT CAPACITIES OF SATURATED LIQUIDS USING THE YUAN-STIEL METHOD[5]

	T_r			
	0.5	0.6	0.7	0.85
Ammonia	20.5	19.6	19.9	21.9
Methylamine	23.7	23.3	24.2	27.4
Ethylamine	29.6	30.0	31.8	36.3
R-22	21.8	22.1	23.1	27.5
R-21				
Ethylene glycol	58.5	54.6	55.2	62.5
1,4-Butanediol	90.2	83.9	85.4	96.9
DGDE	63.4	67.9	73.6	84.0
DMA	44.3	47.2	51.3	58.9
DMH	74.3	80.4	88.0	101
DMD	108	117	128	146

Table 22

ESTIMATION OF THE ENTHALPY OF VAPORIZATION[5] (ΔH_v^b), k_{cal} mol^{-1}) THE BOILING POINT

	Experimental	Estimated	Percent Difference
Ammonia	5.5827	5.704	2.2
Methylamine	6.169	6.097	-1.2
Ethylamine	6.53	6.409	-1.9
R-22	4.8325	4.844	0.2
Ethylene glycol	NA	15.6	
1,4-Butanediol	NA	15.9	
DGDE	NA	10.1	
DMA	NA	9.7	
DMH	NA	11.2	
DMD	NA	13.1	
		Avg	1.4

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