I LATENT HEAT OF VAPORIZATION OF n-HEXANE

II VOLUMETRIC AND LATENT HEAT OF VAPORIZATION MEASUREMENTS FOR TRANS-2-BUTENE

III PARTIAL ENTHALPY CHANGE UPON VAPORIZATION FOR n-BUTANE IN THE n-BUTANE-n-DECANE SYSTEM

Thesis by

Johannes Huisman

In Partial Fulfillment of the Requirements
For the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1964
(Submitted May 8, 1964)

ACKNOWLEDGMENTS

I wish to express my deep gratitude to Professor Bruce H. Sage, under whose direction this research was conducted, for his guidance and advice.

Many people contributed to this work and their assistance is greatly appreciated. Harold T. Couch introduced me to the calorimeter operating techniques. Henry E. Smith assisted with the calorimetric measurements and Harry C. Wiese assisted with the volumetric work. I wish to thank H. Hollis Reamer for his cooperation and assistance. The contributions of Willard M. Dewitt, George A. Griffith, Paul B. Holmen, Lee T. Carmichael, Dennis J. Graue, Virginia Berry, B. Lawson Miller and others are gratefully acknowledged.

I am indebted to Professor William H. Corcoran for his advice on graduate research. I owe much to my wife Kitty for assisting with some of the experimental work and for typing this Thesis.

I wish to acknowledge with gratitude the financial support of the experimental work by the Standard Oil Company of California who also made me the recipient of a fellowship. Much of the apparatus used in this work was made available by the Jet Propulsion Laboratory of the California Institute of Technology.

ABSTRACT

I. The enthalpy change upon vaporization of n-hexane was experimentally determined by calorimetric measurements at temperatures between 100° and 340°F. The results are presented in tabular and graphical form. Good agreement is indicated with the limited data available.

II. The specific volumes of the liquid and dense phase of trans-2-butene were measured at pressures up to 5000 pounds per square inch in the temperature interval between 40° and 400°F. The latent heat of vaporization was determined from calorimetric measurements at temperatures between 100° and 250°F. The results are presented in graphical and tabular form together with comparisons with earlier published data.

III. The enthalpy change upon vaporization, often referred to as the differential latent heat of vaporization, has been measured for the n-butane-n-decane system by calorimetric techniques. The measurements covered the complete composition range in the temperature interval between 100° and 340°F. The partial enthalpy change upon vaporization for n-butane was determined by applying a correction for the presence of small amounts of n-decane in the vapor. The partial internal energy change upon vaporization for n-butane was also computed. The results are presented in graphical and tabular form. A general thermodynamic analysis for withdrawal or addition of material to an isochoric vessel containing coexisting phases of a multicomponent system is presented.

TABLE OF CONTENTS

PART I LATENT HEAT OF VAPORIZATION OF n-HEXANE PAGE

PART II VOLUMETRIC AND LATENT HEAT OF VAPORIZATION MEASUREMENTS FOR TRANS-2-BUTENE

TABLE OF CONTENTS Ctd.

PART III PARTIAL ENTHALPY CHANGE UPON VAPORIZATION FOR n-BUTANE IN THE n-BUTANE-n-DECANE SYSTEM

PAGE

TABLE OF CONTENTS Ctd.

PART III Ctd. PAGE

PART I

LATENT HEAT OF VAPORIZATION OF n-HEXANE

LATENT HEAT OF VAPORIZATION OF n-HEXANE *

John Huisman and B. H. Sage

Chemical Engineering Laboratory
California Institute of Technology
Pasadena, California

INTRODUCTION

Limited calorimetric measurements of the latent heat of vaporization of n-hexane over a range of temperatures appear to be available. Waddington and Douslin (10) measured values of the latent heat of vaporization at temperatures between 77° and 156°F. Both Young (12) and Kay (2) measured the vapor pressure and the specific weight of the saturated liquid and gas from 140° to 455°F. Values of vapor pressures and latent heat of vaporization are also available from a recent correlation (1). Stewart and co-workers (9) reported values of the specific weight of the liquid. Thermodynamic properties of n-hexane have been reported by Weber (11). In the latter work the latent heats of vaporization of Waddington and Douslin (10) were used at temperatures between 77° and 156°F and the Clapeyron equation was employed at other temperatures. The present investigation involves calorimetric measurements of the latent heat of vaporization of n-hexane at temperatures between 100° and 340°F.

---

* Reprinted from the Journal of Chemical and Engineering Data, Vol. 9, No. 2, Page 223, April, 1964. Copyright 1964 by the American Chemical Society and reprinted by permission of the copyright owner.

METHODS

The experimental apparatus employed in this investigation has been described in some detail (4,7). Principles and methods are similar to those developed by Osborne and co-workers (5,6). An isochoric vessel containing a heterogeneous mixture of n-hexane was located within an adiabatic vacuum jacket. A mechanical agitator and electrical heater were provided within the isochoric vessel. The n-hexane was withdrawn as a gas and the quantity withdrawn determined by conventional weighing bomb techniques (8). A detailed thermodynamic analysis of the process is available (3,4) which permitted the minor digressions from isobaric, isothermal conditions during the evaporation to be taken into account. Corrections were applied for mechanical energy added to the system as a result of the agitation of the liquid phase and the minor thermal transfers between the calorimeter and the nearly adiabatic jacket. The fact that the gas phase was withdrawn form the isochoric chamber at a slightly different temperature than the evaporating liquid temperature was also taken into account. It is beyond the scope of this discussion to review the thermodynamic analysis (3,4) of the process.

The latent heat of vaporization under idealized isobaric, isothermal conditions is given by the following expression :

$$\ell = (H_g - H_\ell) = [Q]_{T,P} \left(\frac{V_g - V_\ell}{V_g} \right) \qquad (1)$$

where the quantity $[Q]_{T,P}$ represents the net energy required per unit weight of material withdrawn from the isochoric calorimeter under isothermal conditions.

In the current measurements the deviations from idealized isobaric, isothermal conditions did not introduce corrections to the latent heat of vaporization of more than 0.3%. The energy associated with the agitation was less then 1.3% of the electrical energy input at all states investigated. The estimated uncertainties of the several variables associated with measurements of the enthalpy change upon vaporization of n-hexane are set forth in Table I. The information in Table I is presented in terms of the fraction of the measured enthalpy change upon vaporization of n-hexane at a temperature of 280° F.

Equation 1 indicates that a knowledge of the volumetric behavior of the coexisting liquid and gas phases is necessary even under idealized conditions in order to relate the measured energy input $[Q]_{T,P}$ to the latent heat of vaporization . It appeared desirable to eliminate the use of directly measured specific volumes of the saturated gas since these are subject to uncertainties as the result of adsorption.

By combining the Clapeyron equation with Equation 1, the latent heat of vaporization of n-hexane may be evaluated in the following way:

$$\ell = [Q]_{T,P} - V_\ell \, T \, (dP''/dT) \tag{2}$$

In the application of Equation 2 the volumetric measurements of Stewart (9) were employed to establish the specific volume of the saturated liquid as a function of temperature. The vapor pressure measurements reported by Young (12) as well as values submitted in a critical review (1) were employed in the present measurements to evaluate the quantity dP"/dT. Residual techniques were employed in these operations and it is believed that the derivative dP"/dT does not involve uncertainties of more than 0.2% from the measured values of vapor pressure reported (1). The specific volume of the dew-point gas was evaluated from the current measurements of the latent heat of vaporization by application of the Clapeyron equation :

$$V_g = V_\ell + \frac{\ell}{T\,(dP''/dT)} \qquad (3)$$

MATERIALS

The n-hexane utilized in this experimental investigation was obtained as research grade from the Phillips Petroleum Co. which reported it to contain not more than 0.0004 mole fraction of impurities. The specific weight of the material was 40.881 pounds per cubic foot at 77°F which compared with a value of 40.878 pounds per cubic foot reported (1) for an air-saturated sample at the same temperature. Measurements of the index of refraction relative to the D-lines of sodium at 77°F indicated an index of 1.3723 as compared to a value of 1.37226 reported (1) for an air-saturated sample at the same temperature. A review of these data leads the authors to believe that the sample of n-hexane employed had a purity of at least 0.9996 mole fraction. The probable impurities are isomers of this hydrocarbon. It should be recognized that traces of impurities in calorimetric measurements of the latent heat of vaporization do not introduce uncertainties of the same magnitude as similar quantities of impurities would in the case of volumetric or vapor pressure measurements.

EXPERIMENTAL RESULTS

The results of the experimental measurements upon n-hexane are reported in Table II. It should be recognized that an error of 1% in the slope of the vapor pressure curve which is recorded in Table II introduces less than 0.08% uncertainty in the measured enthalpy change at the highest temperature recorded. The specific volume at dew point was calculated by application of Equation 3 and the compressibility factor recorded was evaluated, employing a molecular weight of n-hexane of 86.172 and a value of the universal gas constant of $R = 10.73147$ (psi)(cu ft)/(lb-mol)($^{\circ}$R). Values of the latent heat of vaporization recorded in Table II are represented in Figure 1. Critically chosen values (1) have been included for comparison.

In order to permit a more precise comparison of the present measurements with data reported by other investigators, residual techniques were employed. In the present instance, the residual latent heat of vaporization has been calculated by the following expression :

$$\underset{\sim}{\ell} = \ell - (173.00 - 0.22\, t) \qquad (4)$$

Values of the residual latent heat of vaporization obtained in the present measurements are set forth in Figure 2 along with critically chosen values (1) and the experimental measurements of Waddington and Douslin (10). The "standard error of estimate" of the current measurements of the latent heat of vaporization from the smooth curve shown in Figure 2 was 0.21 Btu per pound. This measure of uncertainty is defined by :

$$\sigma = \left[\left\{ \sum^{N} (x_e - x_s)^2 \right\} \Big/ (N - 1) \right]^{1/2} \qquad (5)$$

In Equation 5, σ is the standard error of estimate, x_e the experimental value, x_s the smooth value, and N the number of experimental points. The corresponding measure of uncertainty of the experimental work of Waddington and Douslin (10) was 0.58 Btu per pound. Smooth values of the latent heat of vaporization are reported as a function of temperature in Table III. The internal energy change upon vaporization and the specific volume at dew point are presented also.

The compressibility factor for the dew-point or saturated gas as a function of pressure is shown in Figure 3. The standard error of estimate of the experimental values of the compressibility factor of the dew-point gas recorded in Table II from the smooth curve shown in Figure 3 is 0.0017. As a matter of interest, the compressibility factor calculated from the directly measured values of the specific volume of the dew-point gas as reported by Young (12) has been included for comparison. These data indicate a standard error of estimate of the experimental values reported by Young (12) of 0.0072 from the smooth curve. Likewise, the values of the compressibility factor calculated from the more recent compilation of the thermodynamic properties of n-hexane by Weber (11) have been included. It is understood that the specific volumes of the dew-point gas reported by Weber (11) were at least in part based on the data of Young (12). The standard error of estimate of the values tabulated by Weber from the smooth curve shown in Figure 3 is 0.0063.

ACKNOWLEDGMENT

The experimental work reported was carried out with the financial support of the Standard Oil Company of California which made available a fellowship to Mr. Huisman. The calorimetric equipment was originally constructed through the support of the Jet Propulsion Laboratory of this Institute by Project MX-121 of the Air Material Command and by the Ordinance Department. Virginia Berry contributed to the calculation of the experimental results and B. Lawson Miller to the preparation of the manuscript.

LITERATURE CITED

1. American Petroleum Research Project 44, Petrol. Res. Lab., Carnegie Inst. Technol., "Selected Values of Properties of Hydrocarbons and Related Compounds".
2. Kay, W. B., J. Am. Chem. Soc., 68, 1336 (1946).
3. McKay, R. A., Sage, B. H., Am. Doc. Inst., Washington, D. C., Doc. No. 6072 (1959).
4. McKay, R. A., Sage, B. H., J. Chem. Eng. Data, 5, 21 (1960).
5. Osborne, N. S., Stimson, H. F., Flock, E. F., Bur. Standards J. Research, 5, 411 (1930).
6. Osborne, N. S., Stimson, H. F., Ginnings, D. C., J. Research Natl. Bur. Standards, 23, 197 (1939).
7. Sage, B. H., Hough, E. W., Anal. Chem., 22, 1304 (1950).
8. Sage, B. H., Lacey, W. N., Trans. Am. Inst. Mining Met. Engrs., 136, 136 (1940).
9. Stewart, D. E., Sage, B. H., Lacey, W. N., Ind. Eng. Chem., 46, 2529 (1954).
10. Waddington, Guy, Douslin, D. R., J. Am. Chem. Soc., 69, 2275 (1947).
11. Weber, J. H., A.I.Ch.E. Journal, 2, 514 (1956).
12. Young, Sidney, Sci. Proc. Roy. Dublin Soc., 12, 374 (1909-10)

NOMENCLATURE

d	differential operator
ℓ	latent heat of vaporization, Btu/lb
$\underset{\sim}{\ell}$	residual latent heat of vaporization, Btu/lb
H	enthalpy, Btu/lb
P''	vapor pressure, psia
$[Q]$	heat added per unit weight of material withdrawn under idealized conditions, Btu/lb
T	thermodynamic temperature, °R
t	temperature, °F
V	specific volume, cu ft/lb

Subscripts

g	gas phase
ℓ	liquid phase
P	pressure
T	temperature

LIST OF FIGURES

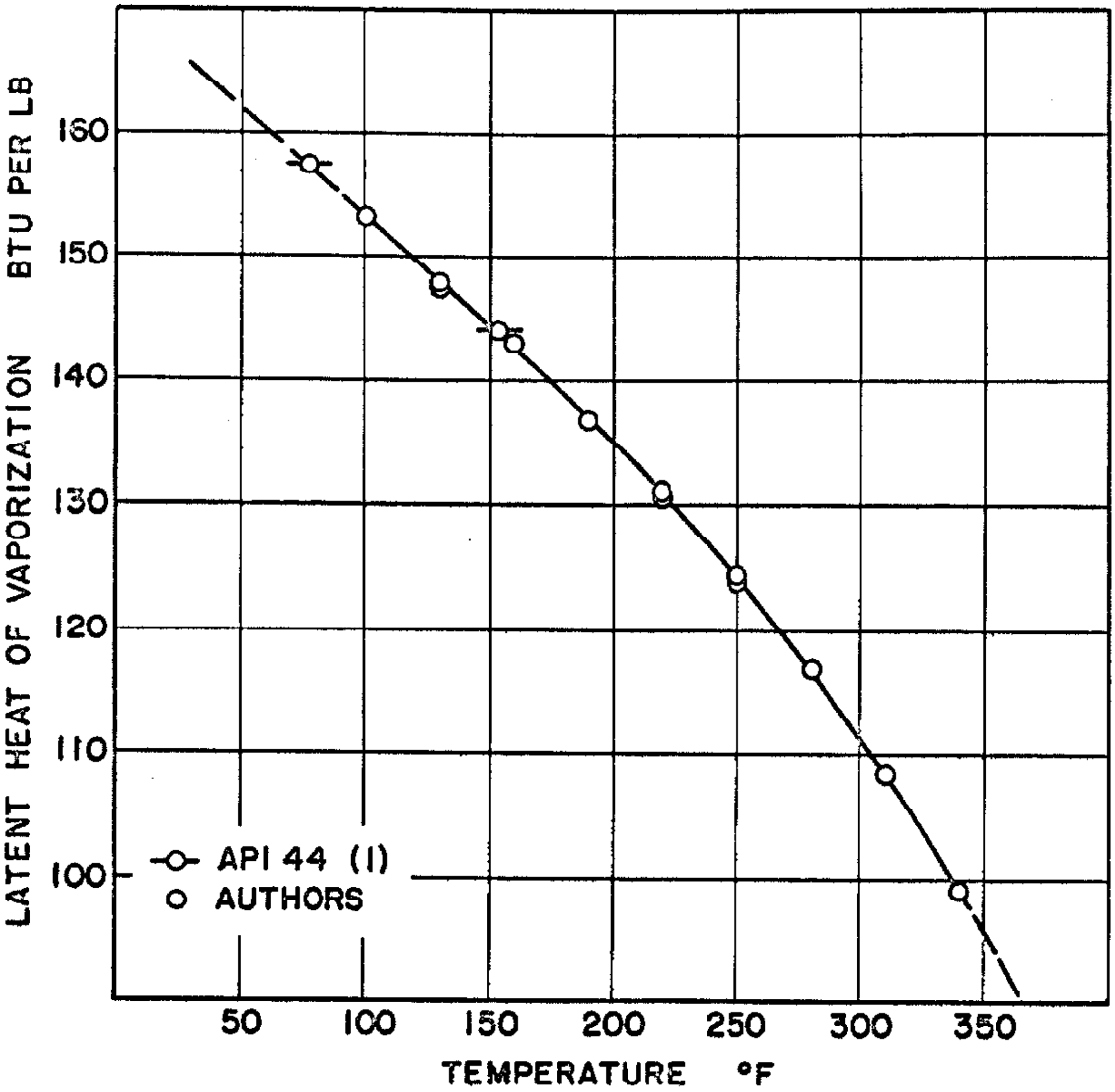

Fig. 1. Latent Heat of Vaporization for n-Hexane

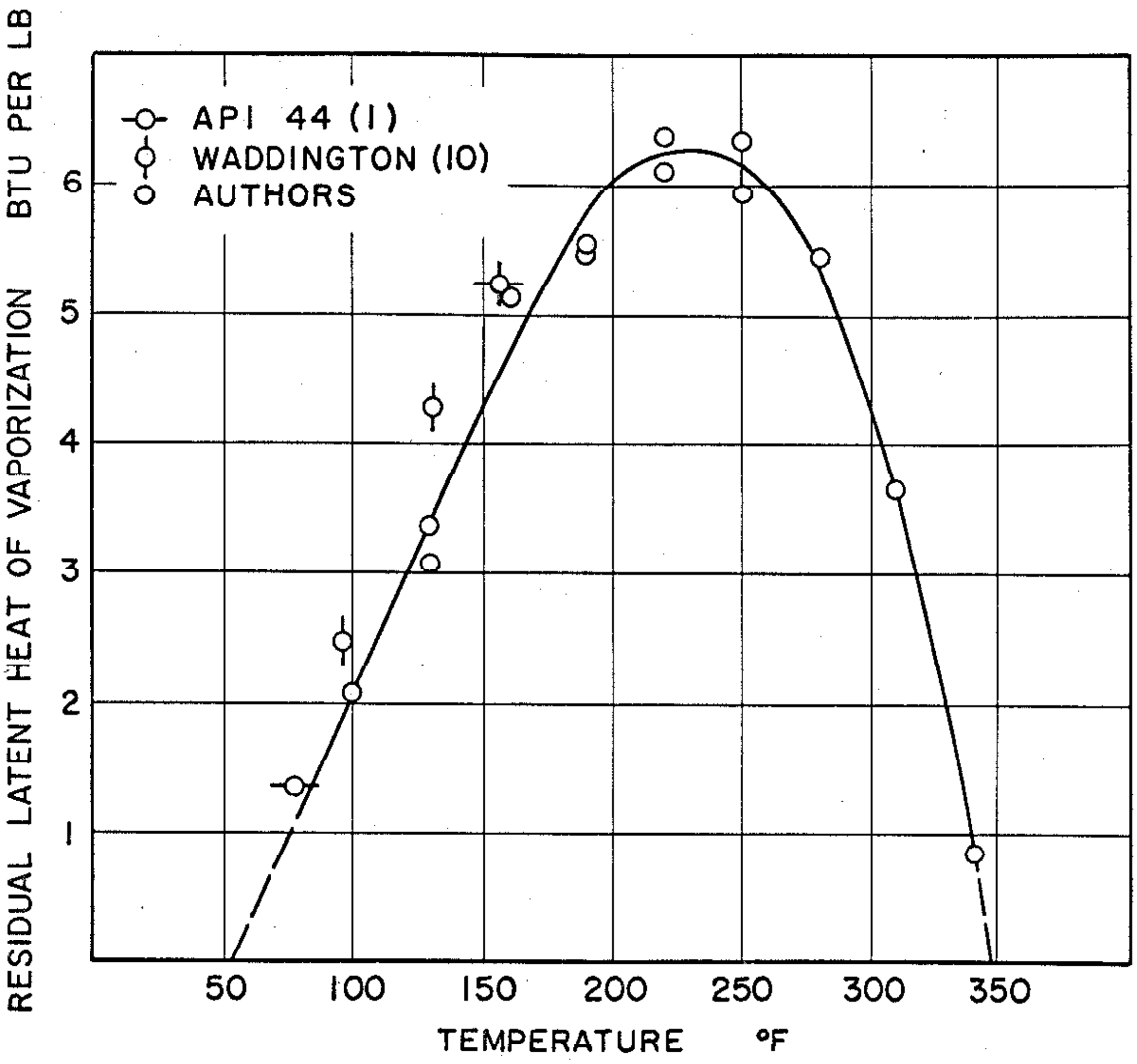

Fig. 2. Residual Latent Heat of Vaporization

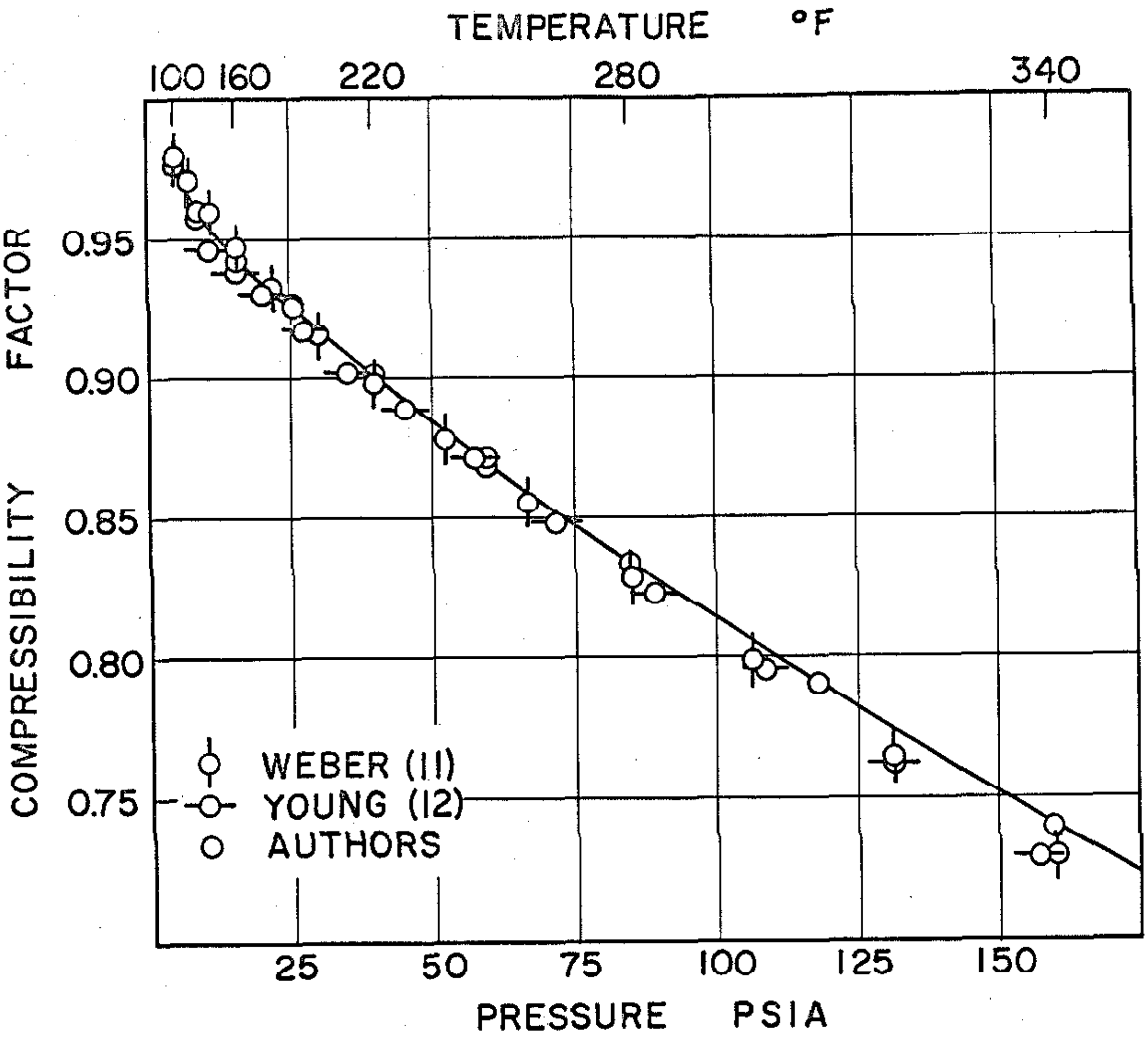

Fig. 3. Compressibility Factor for Dew-Point Gas

LIST OF TABLES

TABLE I

ESTIMATED UNCERTAINTIES OF MEASUREMENT

Quantity	Probable Uncertainty per cent
Energy added electrically	0.03
Energy added by agitation	0.15
Energy exchange between calorimeter and jacket	0.03
Change in temperature of liquid and vapor	0.03
Weight of material withdrawn	0.02
Volumetric correction factor	0.05
Superheat of liquid	0.04

TABLE II

EXPERIMENTAL RESULTS FOR n-HEXANE

Identification	Temperature °F	Pressure[a] P.S.I.A.	Energy Added			Weight of Material Withdrawn lb	Superheat of Liquid °F	dP^*/dT psi/°R	Specific Volume		Compressibility Factor	Volumetric Correction Factor[b]	Latent Heat of Vaporization Btu/lb
			Electrically Btu	By Agitation Btu	By Conduction and Radiation Btu				Dew Point cu ft/lb	Bubble Point[a] cu ft/lb			
382	100	4.95	5.3126	0.0887	-0.0017	0.035224	0.15	0.1077	13.75	0.02493	0.9764	0.99819	153.08
384	130	9.16	5.3946	0.0773	-0.0023	0.036916	0.17	0.1765	7.696	0.02553	0.9600	0.99669	147.74
386	130	9.16	5.3818	0.0828	-0.0016	0.037931	0.19	0.1765	7.682	0.02553	0.9582	0.99668	147.46
396	160	15.82	5.5704	0.0830	-0.0014	0.039344	0.16	0.2728	4.594	0.02618	0.9418	0.99430	142.91
388	190	25.76	5.2113	0.0764	0.0047	0.038383	0.12	0.3948	2.906	0.02691	0.9253	0.99074	136.67
389	190	25.76	3.7980	0.0556	0.0003	0.027936	0.11	0.3948	2.908	0.02691	0.9257	0.99075	136.73
390	220	39.87	2.4040	0.0491	-0.0029	0.018468	0.10	0.5521	1.910	0.02775	0.8996	0.98544	130.70
391	220	39.87	3.9475	0.0804	0.0090	0.030386	0.09	0.5521	1.914	0.02775	0.9015	0.98547	130.97
393	250	59.24	3.4772	0.0413	-0.0007	0.027772	0.12	0.7450	1.295	0.02868	0.8683	0.97784	123.93
398	250	59.24	5.5968	0.0570	-0.0032	0.044467	0.12	0.7450	1.299	0.02868	0.8710	0.97791	124.33
400	280	84.93	6.4212	0.0435	-0.0030	0.053526	0.15	0.9755	0.9047	0.02977	0.8341	0.96706	116.83
402	310	118.2	4.0326	0.0456	0.0010	0.035810	0.07	1.2484	0.6408	0.03103	0.7902	0.95162	108.43
405	340	160.3	5.3351	0.0404	-0.0016	0.050426	0.06	1.5681	0.4594	0.03256	0.7395	0.92904	99.05

[a] Stewart et al (9).

[b] Not used directly in evaluation of latent heat of vaporization.

TABLE III

CRITICALLY CHOSEN VALUES OF SOME PROPERTIES OF n-HEXANE

Temp. °F	Specific Vol. at Dew Point cu ft/lb	Internal Energy Change on Vaporization Btu/lb	Latent Heat of Vaporization Btu/lb
50	42.90	150.30	161.90
60	33.73	148.35	160.15
70	26.45	146.36	158.37
80	21.09	144.41	156.60
90	16.80[a]	142.44	154.80[a]
100	13.71	140.55	153.08
110	11.21	138.61	151.31
120	9.290	136.70	149.56
130	7.699	134.78	147.79
140	6.474	132.88	146.03
150	5.460	130.99	144.27
160	4.605	129.11	142.51
170	3.922	127.21	140.73
180	3.348	125.30	138.90
190	2.902	123.29	137.00
200	2.495	121.23	135.02
210	2.187	119.10	132.96
220	1.913	116.94	130.85
230	1.684	114.73	128.67
240	1.488	112.48	126.43
250	1.299	110.20	124.13
260	1.152	107.87	121.76
270	1.019	105.48	119.31
280	0.9046	103.03	116.78
290	0.8109	100.50	114.14
300	0.7109	97.87	111.37
310	0.6406	95.10	108.43
320	0.5742	92.25	105.40
330	0.5102	89.37	102.28
340	0.4594	86.39	99.05
350	0.4139	83.34	95.73

---

[a] Values at this and lower temperatures extrapolated from data at higher temperatures.

PART II

VOLUMETRIC AND LATENT HEAT OF VAPORIZATION MEASUREMENTS FOR TRANS-2-BUTENE

VOLUMETRIC AND LATENT HEAT OF VAPORIZATION MEASUREMENTS FOR TRANS-2-BUTENE *

John Huisman and B. H. Sage

Chemical Engineering Laboratory
California Institute of Technology
Pasadena, California

INTRODUCTION

The thermodynamic properties of trans-2-butene have not been studied in great detail. Lamb and Roper (8) measured the vapor pressure of this compound at temperatures between -91° and 49°F. while Kistiskowsky (7) reported values at temperatures from -108° to 76°F. Guttman and Pitzer (4) measured the vapor pressure of trans-2-butene at temperatures between -96° and 34°F and also determined the latent heat of vaporization of this compound at a temperature in the vicinity of 34°F. The specific weight of the bubble-point liquid has been reported (1). The available experimental information did not seem sufficient to establish with certainty the volumetric behavior in the liquid phase nor the latent heat of vaporization of this compound. For this reason measurements were made of the volumetric behavior of the liquid phase at pressures up to 5000 pounds per square inch in the temperature interval between 40° and 400°F and of the latent heat of vaporization at temperatures between 100° and 250°F.

---

* Submitted for publication to the Editor of Journal of Chemical & Engineering Data.

MATERIALS

The trans-2-butene employed for both the volumetric and calorimetric measurements was obtained from the Phillips Petroleum Co. and was reported to obtain less than 0.2 mole per cent of impurity. After appropriate deaeration the sample showed less than 0.25 pound per square inch variation in vapor pressure with change in quality from 0.1 to 0.9 at 160°F.

VOLUMETRIC MEASUREMENTS

Utilizing available pressure-volume-temperature equipment, the volumetric behavior of trans-2-butene in the liquid phase was established. In principle, the apparatus involved a stainless steel pressure vessel within which a sample of known weight was confined over mercury. The effective volume of the system was varied by the introduction or withdrawal of mercury and the resulting equilibrium pressure was measured. The attainment of physical equilibrium was hastened by the use of a mechanical agitator. The temperature of the vessel was known within 0.05°F relative to the international platinum scale. Pressures were determined by means of a balance (13) with an uncertainty of 0.1 pound per square inch or 0.03%, whichever was the larger measure of uncertainty. The volumes occupied by the hydrocarbon system were known within 0.25% throughout the entire range of pressures and temperatures covered by this investigation. The weight of the hydrocarbon employed was determined by gravimetric methods and the sample was introduced into the pressure-volume-temperature equipment by conventional weighing bomb techniques (13). A detailed description of this equipment and the methods employed is available (13).

The results of the experimental measurements at eigh temperatures between 40° and 400°F are set forth in Table I. The corresponding measurements of vapor pressure at these temperatures constitute Table II. The experimental volumetric measurements are portrayed graphically in Figure 1. The standard error of estimate of the experimental data from the smooth curves was 1.3 x 10^{-5} cubic foot per pound. The vapor pressure of trans-2-butene may be described approximately by

$$\log P_r'' = 5.62209 - \left(\frac{2206.093}{T}\right) \tag{1}$$

Utilizing this as a reference, the residual vapor pressure may be defined as

$$\underset{\sim}{P}'' = P_r'' - P'' \tag{2}$$

The residual vapor pressure is shown as a function of temperature in Figure 2. Included also are the API 44 (1) critically chosen values and those reported by other investigators (3,4,7,8). The standard error of estimate (6) of the current data from the smooth curve shown in Figure 2 was 0.06 pound per square inch. The data of API 44 (1) and Guttman and Pitzer (4) yielded a standard error of estimate of 0.02, while those reported by Kistiakowsky and co-workers (7) and Lamb and Roper (8) indicated a standard error of 0.03 and 0.04 pound per square inch, respectively. The data of Cragoe (3) deviated from the present measurements at temperatures above 80°F. From the data reported in Table I and Table II, tempered by the vapor pressure measurements of other investigators (1,4,7,8) the specific volume of trans-2-butene in the liquid and dense phases is set forth in Table III.

LATENT HEAT OF VAPORIZATION MEASUREMENTS

The latent heat of vaporization of trans-2-butene was determined by calorimetric techniques at temperatures between 100° and 250°F. In principle, the equipment consists of an isochoric vessel within which the hydrocarbon was confined. An electric heater added energy at a known rate. Physical and thermal equilibrium was approached by means of a mechanical agitator. The gas phase was withdrawn from the calorimeter at a fixed rate and collected in a weighing bomb. From a knowledge of the electrical energy added and the weight of hydrocarbon removed together with the necessary volumetric corrections, the latent heat of vaporization was evaluated (9,10). The details of the equipment employed and the methods utilized are available (10.12).

As the temperature is increased the magnitude of the volumetric correction becomes greater. As a result, the use of such calorimetric techniques for the evaluation of the enthalpy change upon vaporization becomes less accurate as the critical state is approached. For this reason no effort was made to carry the measurements above 250°F., although the equipment will permit measurements at temperatures as high as 340°F.

The experimental measurements associated with the latent heat of vaporization of trans-2-butene are set forth in Table IV. The pertinent experimentally measured quantities and the associated corrections have been included. The volumetric correction (2) was established from the specific volume of the bubble-point liquid, the temperature, and the slope of the vapor pressure curve. The latent heat of vaporization as measured under idealized (2) isobaric, isothermal conditions is related to the measured thermal quantities by

$$\ell = (H_g - H_\ell)_T = [Q]_{T,P} - V_\ell T(dP''/dT) \qquad (3)$$

The magnitude of the volumetric correction term $V_1T(dP''/dT)$ is set forth in Figure 3 and is recorded in a part of Table IV. The estimated uncertainties of measurement associated with the investigation of the latent heat of vaporization are set forth in Table V. The greatest uncertainty lies in the evaluation of the energy added by agitation followed by the determination of the volumetric correction term.

The latent heat of vaporization which is recorded in a part of Table IV is portrayed graphically in Figure 4 along with the measurements of Guttman and Pitzer (4) and Kistiskowsky (7), as well as the API 44 (1) critically chosen values. The latent heat of vaporization of trans-2-butene may be approximated by

$$\ell_r = 185 - 0.35\,t \qquad (4)$$

The residual latent heat of vaporization, utilizing Equation 4 as a reference,may be expressed as

$$\underset{\sim}{\ell} = \ell - \ell_r \qquad (5)$$

There is shown in Figure 5 the residual latent heat of vaporization as a function of temperature including the current measurements, the available critically chosen values (1) and the measured values of Guttman and Pitzer (4) and of Kistiskowsky (7). The standard error of estimate of the current experimental data from the smooth curve shown in Figure 5 was 0.13 Btu per pound. The standard error of the values at a single temperature reported by Guttman and Pitzer (4) was 0.1 Btu per pound.

By application of the Clapeyron equation the specific volume of the dew-point gas may be evaluated from

$$V_g = \frac{[Q]_{T,P}}{T\,(dP''/dT)} \tag{6}$$

Likewise, the compressibility factor of the dew-point gas may be established from

$$Z = \frac{P''\,V_g}{b\,T} \tag{7}$$

This factor is shown for the dew-point gas as a function of temperature in Figure 6. The dashed portion of the curve is based on an equation of state of the virial type evaluated by Roper (11). Good agreement between the present values based in part on calorimetric measurements and the values from the equation of state by Roper is apparent. In many ways the use of the Clapeyron equation is the most satisfactory way of determining the volumetric behavior of the dew-point gas at reduced temperatures since direct measurements are fraught with uncertainties associated with adsorption.

From the current measurements, coupled with the available data at lower temperatures (1,11), a set of critically chosen values of the properties of the bubble-point liquid and the dew-point gas are presented in Table VI. In this table the vapor pressure is recorded along with the specific volume of the bubble-point liquid and the dew-point gas and the changes in internal energy and enthalpy associated with vaporization for even values of temperature between 40° and 250°F.

It is estimated that the over-all uncertainty of measurement of the specific volume of the dew-point gas is approximately 0.35% while the internal energy change upon vaporization is known within 0.4% and the enthalpy change upon vaporization within 0.5%.

ACKNOWLEDGMENT

The authors wish to acknowledge the support of the Standard Oil Company of California which provided the fellowship for the senior author during the period this experimental work was being accumulated. Virginia Berry assisted in the preparation of the experimental measurements in a form suitable for publication and B. Lawson Miller with the preparation of the manuscript.

NOMENCLATURE

b	gas constant, (psi) (cu ft)/(lb) (^{o}R)
d	differential operator
H	enthalpy, Btu/lb
ℓ	latent heat of vaporization, Btu/lb
$\underset{\sim}{\ell}$	residual latent heat of vaporization, Btu/lb
P''	vapor pressure, psia
$\underset{\sim}{P''}$	residual vapor pressure, psia
$[Q]_{T,P}$	heat added per unit weight of material withdrawn under idealized conditions, Btu/lb
T	thermodynamic temperature, ^{o}R
t	temperature, ^{o}F
V	specific volume, cu ft/lb
Z	compressibility factor

Subscripts

g	gas phase
ℓ	liquid phase
P	pressure
r	reference
T	temperature

LITERATURE CITED

1. Am. Petroleum Inst. Research Project 44, Petroleum Research Laboratory, Carnegie Institute of Technology, "Selected Values of Properties of Hydrocarbons and Related Compounds."
2. Couch, H. T., Kozicki, William, Sage, B. H., J. Chem. Eng. Data, 8, 346 (1963).
3. Cragoe, C. S., Natl. Bur. Standards, Letter Circular LC-736, Washington, D.C., Nov. 23, 1943.
4. Guttman, Lester, Pitzer, K. S., J. Am. Chem. Soc., 67, 324 (1945).
5. Hackmuth, K. H., Hanson, G. H., Smith, M. L., A.I.Ch.E. Trans., 42, 975 (1946).
6. Huisman, John, Sage, B. H., "Latent Heat of Vaporization of n-Hexane," (in press).
7. Kistiskowsky, G. B., Ruhoff, J. R., Smith, H. A., Vaughan, W. E., J. Am. Chem. Soc., 57, 876 (1935).
8. Lamb, A. B., Roper, E. E., J. Am. Chem. Soc., 62, 806 (1940).
9. McKay, R. A., Sage, B. H., Am. Doc. Inst., Washington, D.C., Doc. No. 6072 (1959).
10. McKay, R. A., Sage, B. H., J. Chem. Eng. Data, 5, 21 (1960).
11. Roper, E. E., J. Phys. Chem., 44, 835 (1940).
12. Sage, B. H., Hough, E. W., Anal. Chem., 22, 1304 (1950).
13. Sage, B. H., Lacey, W. N., Trans. Am. Inst. Mining Met. Engrs., 136, 136 (1940).
14. Smith, C. H., Thodos, George, A.I.Ch.E. Journal, 6, 569 (1960).

LIST OF FIGURES

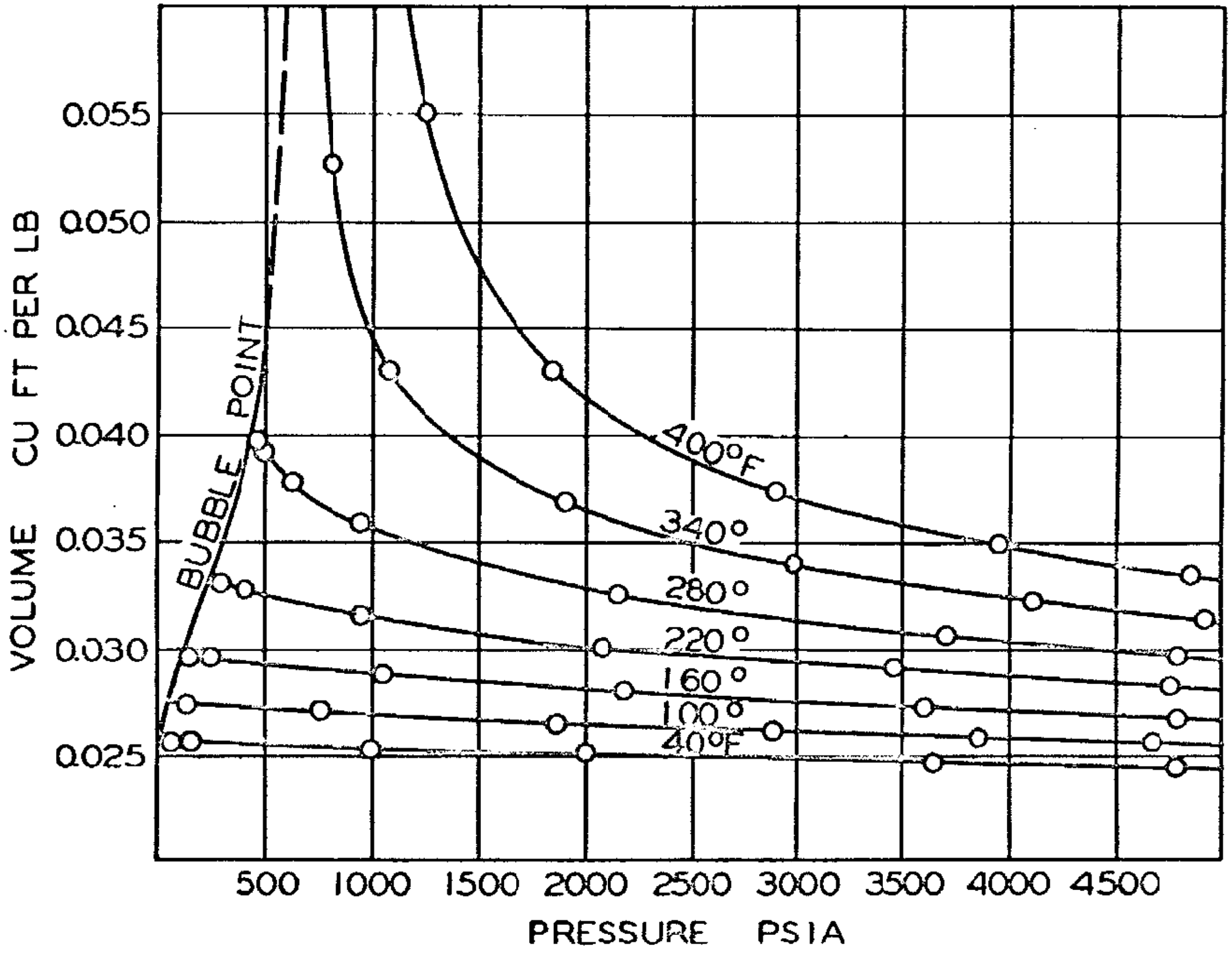

Fig. 1. Specific Volume of Liquid Phase

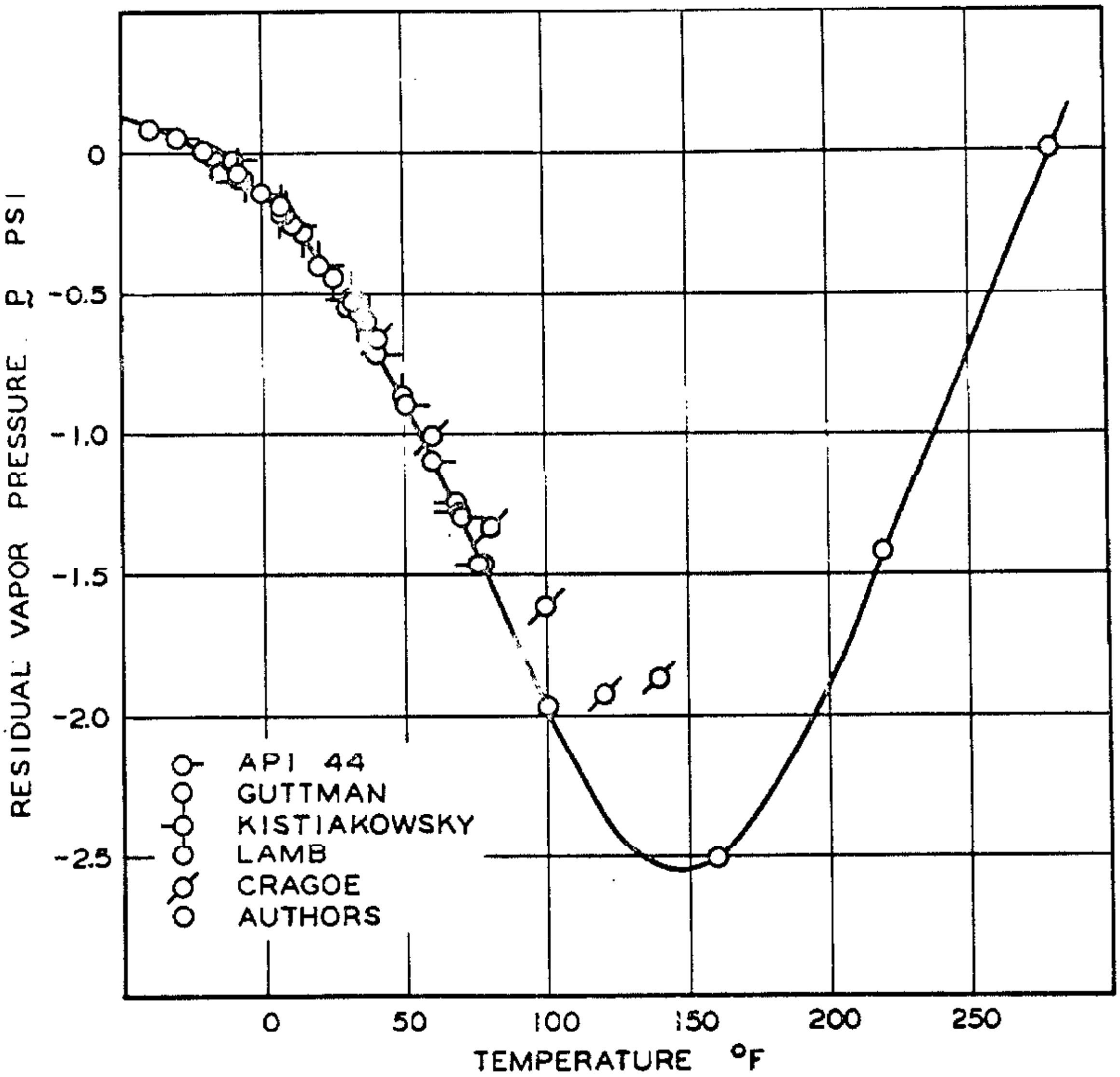

Fig. 2. Residual Vapor Pressure

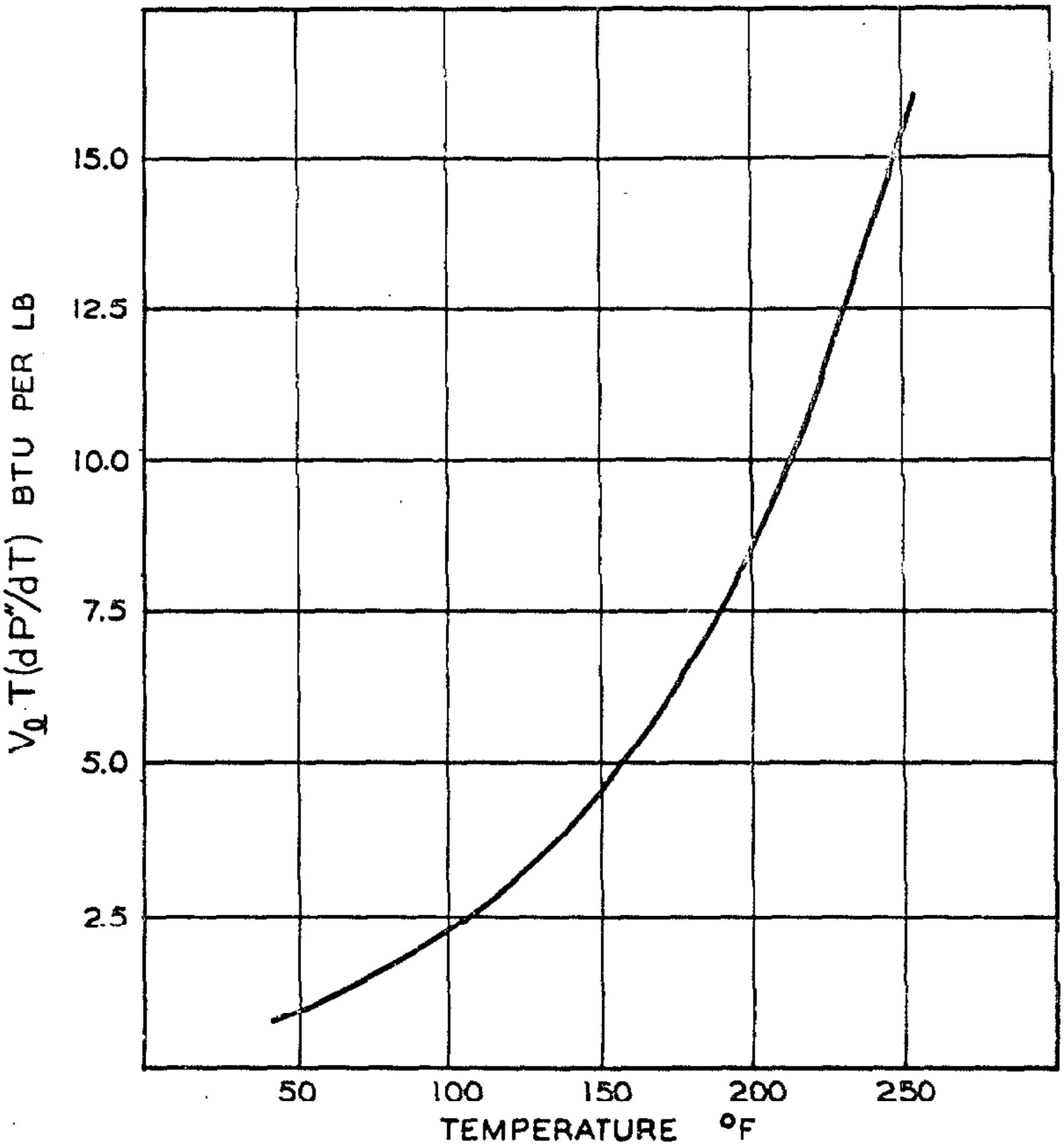

Fig. 3. Volumetric Correction Term

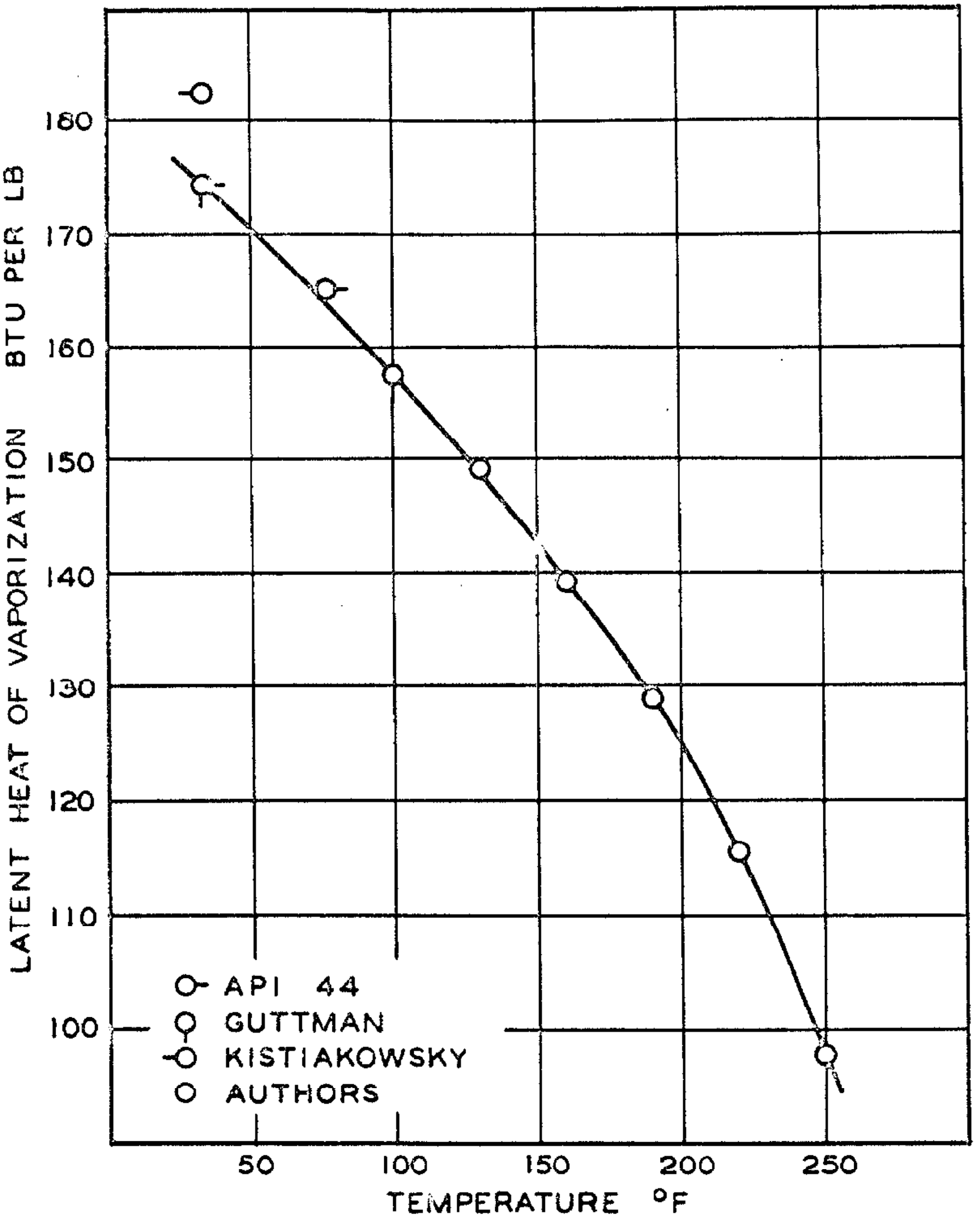

Fig. 4. Latent Heat of Vaporization

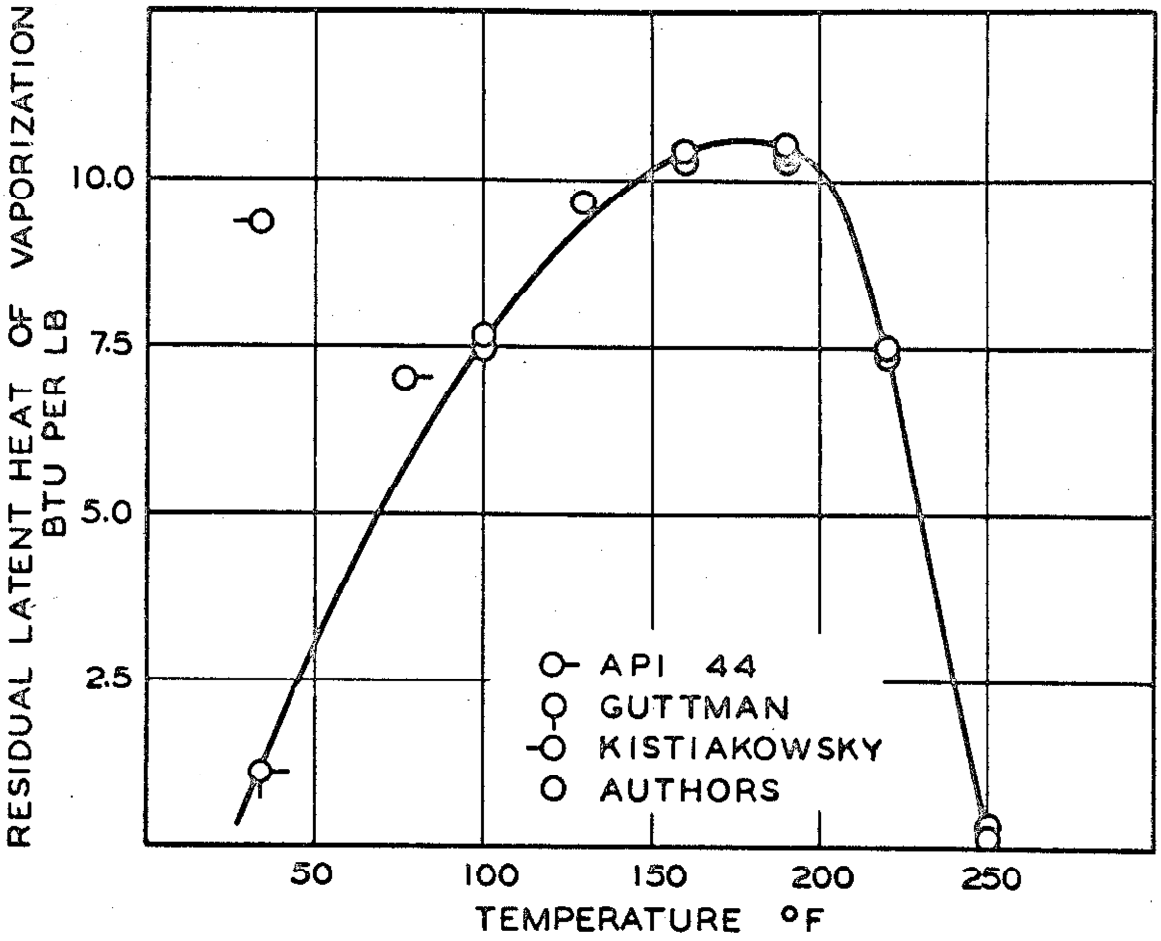

Fig. 5. Residual Latent Heat of Vaporization

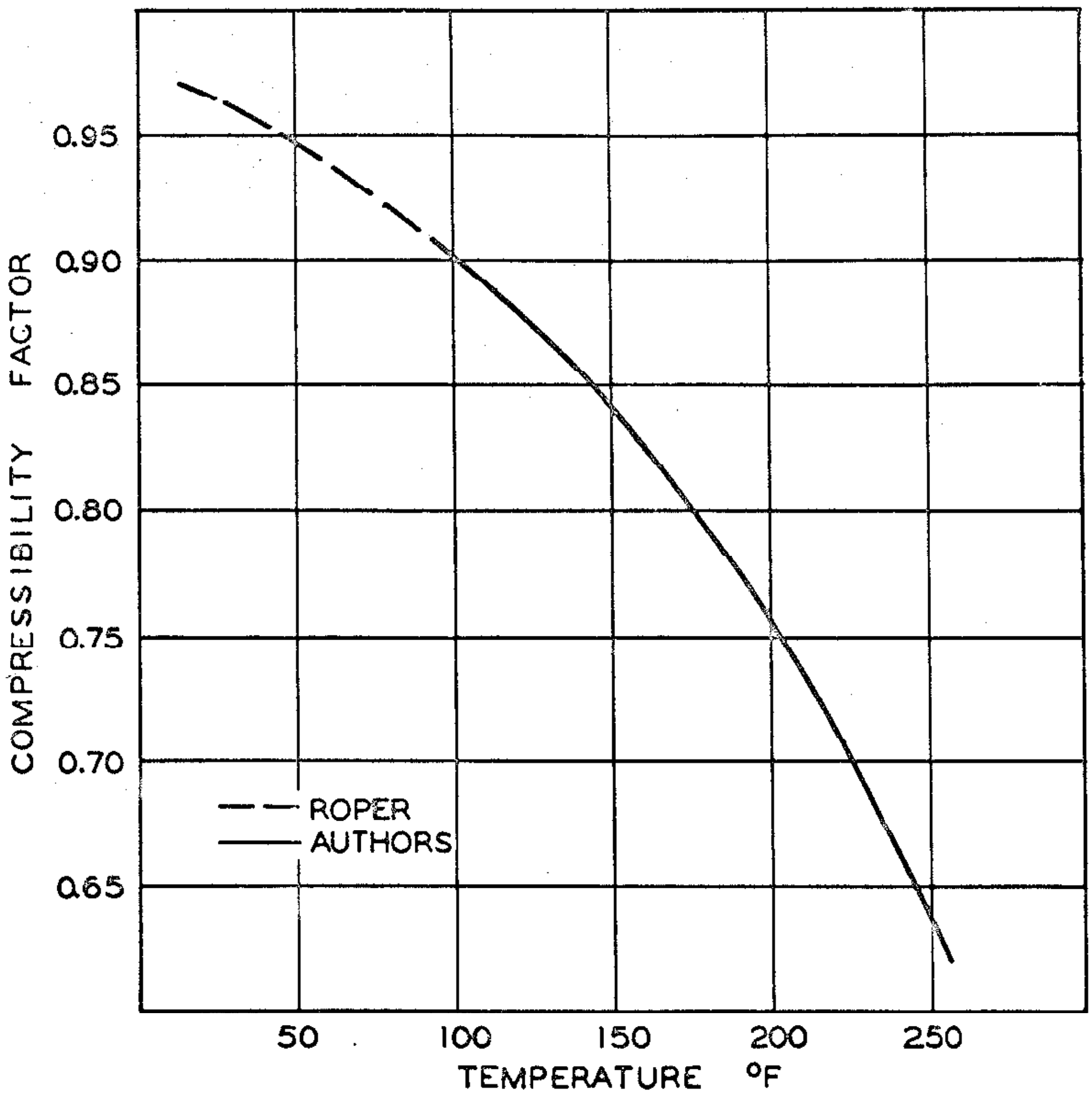

Fig. 6. Compressibility Factor for Dew-Point Gas

LIST OF TABLES

TABLE I. EXPERIMENTAL VOLUMETRIC MEASUREMENTS[a]

Pressure P.S.I.A.	Volume cu ft/lb	Pressure P.S.I.A.	Volume cu ft/lb	Pressure P.S.I.A.	Volume cu ft/lb
40° F.		77° F.		100° F.	
58.8	0.025722	113.8	0.026733	140.4	0.027460
152.9	0.025672	182.0	0.026682	752.0	0.027073
997.7	0.025361	919.9	0.026328	1858.1	0.026510
1994.8	0.025043	1396.8	0.026098	2874.0	0.026083
3637.3	0.024575	2021.6	0.025973	3846.5	0.025809
4749.0	0.024408	3508.7	0.025378	4660.7	0.025564
		4727.0	0.025087		
160° F.		220° F.		280° F.	
138.5	0.029754	283.6	0.033052	456.1	0.039726
247.6	0.029629	401.2	0.032724	486.2	0.039246
1046.0	0.028808	948.4	0.031545	621.7	0.037767
2178.1	0.027961	2076.0	0.030035	936.2	0.035811
3596.3	0.027215	3454.7	0.028905	2150.3	0.032515
4790.5	0.026738	4756.4	0.028170	3698.2	0.030561
				4783.7	0.029691
340° F.		400° F.			
672.8	0.101536	874.6	0.100753		
673.7	0.101177	874.8	0.100741		
717.8	0.076430	998.8	0.076949		
808.9	0.052705	1247.5	0.055121		
1075.4	0.043034	1846.9	0.043018		
1895.3	0.036817	2393.4	0.037326		
2974.7	0.033880	3951.1	0.034784		
4113.5	0.032162	4850.6	0.033358		
4912.6	0.031309				

---

[a] Sample weight 0.276521 lb.

TABLE II. EXPERIMENTAL VAPOR PRESSURE MEASUREMENTS

Pressure P.S.I.A.	Quality	Pressure P.S.I.A.	Quality	Pressure P.S.I.A.	Quality
40° F.		77° F.		100° F.	
16.83[a]		33.93		49.88	
16.96	0.0003	34.10	0.0007	50.11	0.0081
16.94	0.0028	34.09	0.0052	50.03	0.0315
16.91	0.0114	34.05	0.0226	50.00	0.0380
16.90	0.0138	34.03	0.0265	50.13	0.0004
				50.14[b]	0.0004
				50.01[b]	0.0435
160° F.		220° F.		280° F.	
117.89		239.25		436.18	
118.45	0.0036	239.61	0.006	436.62	0.015
118.35	0.0186	239.51	0.030	436.58	0.104
118.37	0.0736	239.30	0.152	436.26	0.361
118.19	0.0865	239.51	0.190	436.28	0.452
		239.58	0.006	436.68	0.015

[a] Chosen value of vapor pressure taken at a quality of 0.5.

[b] Check run.

TABLE III. SPECIFIC VOLUMES IN THE LIQUID PHASE

Pressure P.S.I.A.	Temperature, °F						
	40	100	160	220	280	340	400
Vapor Pressure	16.8[a]	49.9	117.9	239.3	436.2		
Bubble Point	0.02573	0.02748	0.02977	0.03317	0.04004		
200	0.02567[b]	0.02739	0.02968	-	-	-	-
400	0.02560	0.02728	0.02946	0.03274	-	-	-
600	0.02552	0.02716	0.02924	0.03225	0.03800	-	-
800	0.02545	0.02704	0.02904	0.03183	0.03653	0.05340	-
1000	0.02538	0.02693	0.02885	0.03146	0.03554	0.04432	0.07630
1250	0.02529	0.02679	0.02863	0.03106	0.03460	0.04093	0.05500
1500	0.02520	0.02666	0.02843	0.03070	0.03388	0.03894	0.04790
1750	0.02512	0.02654	0.02824	0.03039	0.03329	0.03750	0.04415
2000	0.02504	0.02642	0.02807	0.03012	0.03279	0.03642	0.04175
2250	0.02496	0.02632	0.02791	0.02987	0.03234	0.03560	0.04001
2500	0.02488	0.02621	0.02776	0.02964	0.03194	0.03493	0.03880
2750	0.02481	0.02612	0.02762	0.02944	0.03158	0.03435	0.03782
3000	0.02474	0.02603	0.02749	0.02924	0.03127	0.03384	0.03700
3500	0.02462	0.02586	0.02726	0.02888	0.03073	0.03299	0.03570
4000	0.02451	0.02572	0.02705	0.02855	0.03028	0.03230	0.03470
4500	0.02442	0.02559	0.02685	0.02826	0.02990	0.03174	0.03387
5000	0.02436	0.02547	0.02666	0.02800	0.02954	0.03123	0.03316

[a] Vapor pressure expressed in pounds per square inch absolute.

[b] Volumes expressed in cubic foot per pound.

TABLE IV. EXPERIMENTAL RESULTS FOR LATENT HEAT OF VAPORIZATION

Identification	Temperature °F	Pressure P.S.I.A.	Energy Added			Weight of Material Withdrawn lb	Superheat of Liquid °F	dP"/dT PSI/°R	Compressibility Factor	Specific Volume		Volumetric Term Btu/lb	Latent Heat of Vaporization Btu/lb
			Electrically Btu	By Agitation Btu	By Conduction and Radiation Btu					Dew Point cu ft/lb	Bubble Point cu ft/lb		
413	100	49.90	4.4327	0.1497	-0.0003	0.028689	0.05	0.7986	0.9002	1.931	0.02748	2.27	157.46
414	100	49.90	4.1283	0.0568	-0.0005	0.026178	0.10	0.7986	0.9001	1.933	0.02748	2.27	157.62
411	130	78.52	4.8075	0.1045	0.0005	0.032187	0.09	1.1204	0.8695	1.249	0.02852	3.49	149.17
416	160	117.89	7.2003	0.0750	-0.0002	0.050362	0.10	1.5196	0.8247	0.8292	0.02977	5.19	139.31
417	160	117.89	6.1960	0.1167	-0.0003	0.043663	0.06	1.5196	0.8253	0.8298	0.02977	5.19	139.41
419	190	170.56	4.5620	0.0920	0.0006	0.034121	0.05	2.0108	0.7745	0.5643	0.03125	7.56	128.87
426	190	170.56	6.0161	0.0593	-0.0046	0.044491	0.10	2.0108	0.7749	0.5646	0.03125	7.56	128.93
427	190	170.56	3.6487	0.0361	-0.0027	0.026971	0.10	2.0108	0.7752	0.5648	0.03125	7.56	128.99
420	220	239.32	3.5367	0.0283	0.0169	0.028369	0.06	2.5916	0.7131	0.3874	0.03317	10.81	115.48
421	220	239.32	2.4867	0.0273	-0.0014	0.019919	0.04	2.5916	0.7123	0.3870	0.03317	10.81	115.35
423	250	326.95	5.4756	0.0344	-0.0038	0.048709	0.04	3.2620	0.6356	0.2639	0.03575	15.32	97.74
424	250	326.95	1.6344	0.0833	0.0063	0.015261	0.00	3.2620	0.6351	0.2637	0.03575	15.32	97.65

TABLE V.

ESTIMATED UNCERTAINTIES OF MEASUREMENT

Quantity	Probable Uncertainty per cent
Energy added electrically	0.03
Energy added by agitation	0.10
Energy exchange between calorimeter and jacket	0.01
Change in temperature of liquid and vapor	0.03
Weight of material withdrawn	0.02
Volumetric correction factor	0.08
Superheat of liquid	0.01

TABLE VI.

CRITICALLY CHOSEN VALUES OF SOME PROPERTIES OF trans-2-BUTENE

Temp. °F	Vapor Pressure P.S.I.A.	Specific Volume Bubble Point cu ft/lb	Specific Volume Dew Point cu ft/lb	Internal Energy Change upon Vaporization Btu/lb	Latent Heat of Vaporization Btu/lb
40	16.80	0.02573	5.430	156.05	172.85
50	20.55	0.02600	4.495	153.50	170.50
60	24.90	0.02627	3.753	150.91	168.08
70	29.94	0.02656	3.151	148.27	165.58
80	35.75	0.02685	2.664	145.56	163.00
90	42.39	0.02716	2.263	142.76	160.30
100	49.90	0.02748	1.936	139.89	157.52
110	58.38	0.02780	1.664	137.01	154.68
120	67.89	0.02816	1.437	134.06	151.76
130	78.52	0.02852	1.246	131.11	148.79
140	90.32	0.02892	1.085	128.09	145.74
150	103.4	0.02933	0.9475	125.03	142.60
160	117.9	0.02977	0.8300	121.91	139.37
170	133.8	0.03022	0.7290	118.73	136.03
180	151.4	0.03072	0.6411	115.46	132.56
190	170.6	0.03125	0.5645	112.14	128.97
200	191.6	0.03182	0.4976	108.66	125.18
210	214.5	0.03245	0.4390	104.71	120.84
220	239.3	0.03317	0.3873	99.75	115.43
230	266.4	0.03390	0.3415	94.61	109.77
240	295.5	0.03477	0.3005	89.32	103.85
250	327.0	0.03575	0.2638	83.90	97.70

PART III

PARTIAL ENTHALPY CHANGE UPON VAPORIZATION FOR n-BUTANE IN THE n-BUTANE-n-DECANE SYSTEM

INTRODUCTION

Partial enthalpy changes upon vaporization are of importance in both industrial design calculations and in theoretical understanding of solutions and phase equilibria.

In the design of hydrocarbon-processing units a material balance and an energy balance for a vaporization or condensation process are often required. A material balance calculation requires vapor-liquid equilibrium constants for the individual components of the system and a considerable amount of work has been done in this area. An energy balance requires a knowledge of the partial enthalpy changes upon vaporization. Very little data for the latter property are available. In industrial process calculations it is usually assumed that the partial enthalpy changes are equal to the latent heats of vaporization of the pure components at the same temperature.

The object of this investigation has been to measure the partial enthalpy change upon vaporization for n-butane in the n-butane-n-decane binary system by calorimetric techniques over a range of temperatures and liquid compositions. The results show significant differences between the partial enthalpy change and the latent heat of vaporization for n-butane. As data for other hydrocarbon systems become available in the future, one can expect that some general method for predicting partial enthalpy changes upon vaporization will become apparent.

Method

The following experimental procedure was used in this investigation : An isothermal vaporization process was carried out in a calorimeter containing coexisting liquid and gas phases of the binary system. Material was vaporized by adding electrical energy and withdrawing the gas phase from the calorimeter. The withdrawn material was collected in a chilled weighing bomb. Only two to three per cent of the contents of the calorimeter was withdrawn and consequently the composition and the pressure changed only slightly during the test. A correction was made for the heat associated with the isothermal decrease in pressure.

This method yields the enthalpy change upon vaporization for the binary system. If the system has only one volatile component, the partial enthalpy change upon vaporization for the volatile component is obtained directly. The boiling points of n-butane and n-decane are 31° and 345°F respectively. The n-butane-n-decane system is thus virtually a system with only one volatile component. Only at higher temperatures does the vapor contain appreciable amounts of n-decane. The partial enthalpy change upon vaporization for n-butane at the higher temperatures was obtained by applying a correction for the heat associated with the vaporization of small amounts of n-decane.

McKay (1) carried out a thermodynamic analysis for the vaporization of pure compounds from an isochoric vessel to establish the relation between the enthalpy change upon vaporization and the experimental measurements. A similar analysis was carried out for multicomponent systems for vaporization and condensation processes.

Definitions

The enthalpy change upon vaporization of a pure substance is a well defined quantity. It is also known as the latent heat of vaporization. The corresponding quantity for a component in a mixture is the partial enthalpy change upon vaporization. It is a state property of the two-phase region of a multicomponent system and is thus a function of pressure, temperature and composition. The pressure-composition and the pressure-temperature relations for the two-phase region of a typical binary system are presented in Figure 1. The vapor pressures of the pure component k and j at the temperature T are presented by points 4 and 5 respectively. On the pressure-composition plot the upper line represents the bubble-point pressure of mixtures of components k and j. The lower line represents the dew-point pressure curve. A bubble-point liquid 1 of composition n_1 is in equilibrium with dew-point vapor 2 of composition n_2. The vapor pressure curves of components k and j are shown in the pressure-temperature plot and these curves end in the critical points 11 and 8 respectively. The broken line 8-9-10-11 represents the critical locus for mixtures of j and k. Points 9 and 10 are the critical points for mixtures with compositions n_1 and n_2 respectively.

Let $\bar{H}_{k,g}$ and $\bar{H}_{k,1}$ represent the partial enthalpies of component k in the coexisting gas and liquid phases represented by points 2 and 1 respectively. Then

$$\left(\bar{H}_{k,g} - \bar{H}_{k,\ell}\right) = \Delta \bar{H}_{v,k} \tag{1}$$

is the partial enthalpy change upon vaporization (or condensation) of component k at the two-phase state 1, 2 of the binary system. The quantity $(\bar{H}_{k,g} - \bar{H}_{k,1})$ is equal to the heat associated with the vaporization of unit weight of component k in a frictionless steady state process. The heat associated with the formation of unit weight of vapor in a frictionless steady state evaporation process is given by

$$\left(\bar{H}_{k,g} - \bar{H}_{k,\ell}\right) y_k + \left(\bar{H}_{j,g} - \bar{H}_{j,\ell}\right) y_j =$$

$$\Sigma \left(\bar{H}_{k,g} - \bar{H}_{k,\ell}\right) y_k = \Sigma \ \Delta \bar{H}_{v,k} \, y_k \tag{2}$$

This quantity will be referred to as the enthalpy change upon vaporization. It is a state property of the system just like the partial enthalpy change upon vaporization of a component. The corresponding enthalpy change upon condensation is given by

$$\Sigma \left(\bar{H}_{k,g} - \bar{H}_{k,\ell}\right) x_k = \Sigma \ \Delta \bar{H}_{v,k} \, x_k \tag{3}$$

where the x's are the weight fractions of the components in the bubble-point liquid. The state properties $(\bar{H}_{k,g} - \bar{H}_{k,1})$, $\Sigma (\bar{H}_{k,g} - \bar{H}_{k,1}) \, y_k$ and $\Sigma (\bar{H}_{k,g} - \bar{H}_{k,1}) \, x_k$ are often referred to in the literature as the partial latent heat of vaporization, the differential latent heat of vaporization and the differential latent heat of condensation respectively. The above enthalpy changes upon vaporization are only equal to the heats of vaporization for frictionless steady state processes. The term "enthalpy change" rather than "latent heat" is therefore used in this project. The term "differential" is rather redundant and will not be used here.

The integral isobaric enthalpy change upon vaporization can be defined as the difference in enthalpy of a given composition mixture at dew point and at bubble point for a given pressure. It thus represents the difference between values of the enthalpy at two different states of the system, the composition and the pressure being the same at both states. The integral isobaric enthalpy change upon vaporization can be written as

$$\sum \left(\bar{H}_{k,d} - \bar{H}_{k,b} \right)_{P,n} n_k = \left(H_d - H_b \right)_{P,n} \tag{4}$$

Similarly, the integral isothermal enthalpy change upon vaporization can be written as

$$\sum \left(\bar{H}_{k,d} - \bar{H}_{k,b} \right)_{T,n} n_k = \left(H_d - H_b \right)_{T,n} \tag{5}$$

The isobaric change in state from bubble point to dew point at constant composition is represented on the pressure-temperature plot of Figure 1 by the horizontal line 3-7 for the composition n_2. The corresponding isothermal change in state for composition n_2 is represented by the vertical lines 3-2 on both plots of Figure 1. The above enthalpy changes are often referred to in the literature as the integral isobaric and the integral isothermal latent heats of vaporization. From the following form of the first law of thermodynamics

$$dH = (q + \dot{j}) + V\,dP \tag{6}$$

it is apparent that only for a reversible isobaric process is the enthalpy change equal to the heat. For the corresponding isothermal case the integral of the V dP term from bubble point to dew point must be added to the heat to obtain the integral enthalpy change. This points out that it is thermodynamically not correct to use the term "latent heat" for "enthalpy change" with mixtures. It should be noted that the integral enthalpy change upon vaporization cannot be obtained by integrating the enthalpy change upon vaporization over the path of the change in state. The vapor and liquid phases themselves also undergo enthalpy changes during the process as the pressure or temperature changes from the bubble-point to the dew-point value.

Theoretical Relations

The partial enthalpy change upon vaporization for a component of a multicomponent system can be expressed in terms of other thermodynamic properties of the system by the relation

$$(\bar{H}_{k,g} - \bar{H}_{k,l}) = T(\bar{V}_{k,g} - \bar{V}_{k,l})(\partial P''/\partial T)_x$$

$$+ b_k T^2 \left(\frac{\partial \ln f_{k,g}}{\partial y_k}\right)_{P,T} \left(\frac{\partial y_k}{\partial T}\right)_x \tag{7}$$

It is apparent that calculation of the partial enthalpy change requires a considerable amount of accurate data that is seldom available. For a binary system with only one volatile component the above equation reduces to

$$(\bar{H}_{k,g} - \bar{H}_{k,l}) = T\ (V_g - \bar{V}_{k,l})\ (\partial P''/\partial T)_x \qquad (8)$$

Equations for the enthalpy changes upon vaporization and condensation for multicomponent systems were derived by Kozicki (2) as a proposition :

a For vaporization

$$\Sigma\ (\bar{H}_{k,g} - \bar{H}_{k,l})\ y_k = T\ (\partial P''/\partial T)_x (V_g - \Sigma\ \bar{V}_{k,l}\ y_k) \qquad (9)$$

b For condensation

$$\Sigma\ (\bar{H}_{k,g} - \bar{H}_{k,l})\ x_k = T\ (\partial P''/\partial T)_y \left\{ (\Sigma\ \bar{V}_{k,g}\ x_k) - V_l \right\} \qquad (10)$$

In general these equations can be used to calculate one unknown (e.g. V_g) if accurate values for the other variables are available.

Literature Survey

Very little experimental work has been done to determine partial enthalpy changes upon vaporization. Budenholzer, Sage and Lacey (3) measured values for propane in mixtures with a non-volatile crystal oil at 100°, 160°, and 220°F. Some values for ethane in crystal oil at low ethane concentrations were also determined. The method used was essentially the same as in this investigation, i.e.

isothermal vaporization.

Burrows (4) has correlated some experimental measurements of heats of solution for nitrogen, oxygen and helium in low vapor pressure heavy oils at room temperature. Some values for helium are negative. These heats of solution cannot be classified as partial enthalpy changes upon vaporization, since the solution was not at bubble point. The same applies to the so-called "gas current method" for measuring heats of solution. In this method a steady stream of indifferent gas is bubbled through, or passed over, the solution being investigated. Electrical energy is supplied to make up for the heat associated with vaporization of the volatile component(s). A good description of the procedure and apparatus for this method is given by Hunter and Bliss (5), who measured the heat of vaporization of water from salt solutions.

The enthalpy change upon vaporization $(\sum (\bar{H}_{k,g} - \bar{H}_{k,l})\, y_k)$ was measured by Tyrer (6) for several binary systems at constant atmospheric pressure. It was necessary to measure the heat capacity of the calorimeter system to correct for the temperature increase during the test. For this reason Tyrer selected components that were not more than 14°C apart in boiling point (e.g. acetone-chloroform) to minimize the temperature rise. Even so the temperature rise correction accounted for 7-10 per cent of the enthalpy change upon vaporization. In principle it is better to conduct these experiments under isothermal conditions and apply a correction for the heat effect of the encountered pressure drop. Such a correction is quite small and can be evaluated fairly accurately from available (or estimated) P-V-T data.

It is then not necessary to carry out a heat capacity determination before and after the test.

Stallard and Amis (7) used the gas current method to measure heats of vaporization for the dioxane-water system at 40°C. At this temperature both components are volatile.

Although this project is not directly concerned with integral enthalpy changes upon vaporization, it is of interest to consider the techniques employed in these investigations. Dana (8) measured the integral isobaric enthalpy change upon vaporization of liquid oxygen-nitrogen mixtures at one atmosphere by a steady state non-circulating process. More recent investigators (9,10) used a recirculating flow calorimeter. The compositions of the entering liquid and the leaving vapor are the same, but the temperatures are different. Measured values of the integral isothermal enthalpy change upon vaporization for binary systems are given by Fletcher and Tyrer (11) and Neilson and White (12).

It is significant to note that all the cited investigations, with the exception of the work of Budenholzer et al (3), were carried out at pressures close to atmospheric pressure. The construction of a calorimeter for operation at high pressures is a difficult and expensive project. In this work the encountered pressures ranged from below atmospheric to 300 psi over a temperature range from 100° to 340°F.

THERMODYNAMIC ANALYSIS

The enthalpy changes associated with vaporization or condensation of multicomponent systems can be measured by means of calorimetric techniques. The purpose of this analysis is to derive the relationships that will enable the calculation of these enthalpy changes from experimental measurements.

Consider an isochoric vessel A containing a multicomponent heterogeneous system consisting of a liquid phase and a coexisting gas phase as shown in Figure 2. The calorimeter A is surrounded by an adiabatic jacket B and the space between the calorimeter and the jacket is evacuated. An agitator C and an electrical heater D are provided within the calorimeter. Material may be vaporized by adding energy with the heater and the vapor is withdrawn at point "a". Alternatively gaseous material may be added to the calorimeter at point "a" and condensation will take place at the vapor-liquid interface.

General Differential Equation

The analysis will be carried out in such a way that the results can be applied to either a withdrawal or an addition process. Select as the thermodynamic system the isochoric vessel A and its contents up to withdrawal point "a". The withdrawal or addition process will be treated as an equilibrium process. This can be closely approached in practice by providing efficient agitation and operating at low rates of withdrawal or addition of material. The vapor and liquid phases are thus considered to be in equilibrium at all times. The pressure and temperature are considered to be uniform within the calorimeter.

An energy balance may be written for the system when a differential amount of material dm_a is added or withdrawn at point "a" :

$$d\underline{E} = \underline{q} - \underline{w} + \sum_{k=1}^{\underset{\sim}{n}} \bar{E}_{k,a}\, dm_{k,a} \qquad (11)$$

The thermal transfer term q can be expressed as

$$\underline{q} = q_e + q_s + q_{c+r} \qquad (12)$$

where q_e is the electrical energy input, q_s is the energy input by the stirrer and q_{c+r} is the heat transferred by conduction and radiation from the surrounding vacuum jacket.

Since the vessel A is considered isochoric, the work $\underline{w}$ associated with the process is limited to that concerned with the addition or withdrawal of material :

$$w = -P \sum_{k=1}^{\underset{\sim}{n}} \bar{V}_{k,a}\, dm_{k,a} \qquad (13)$$

The total change in internal energy of the system is the sum of the changes in the internal energy of each of the phases :

$$d\underline{E} = d\underline{E}_g + d\underline{E}_l + d\underline{E}_c \qquad (14)$$

It is desirable to express internal energy in terms of enthalpy :

$$E = H - PV \tag{15}$$

$$d\underline{E}_g = d\underline{H}_g - P\,d\underline{V}_g - \underline{V}_g\,dP \tag{16}$$

$$d\underline{E}_\ell = d\underline{H}_\ell - P\,d\underline{V}_\ell - \underline{V}_\ell\,dP \tag{17}$$

The total enthalpy is a function of P, T and the amount of each component present :

$$\underline{H} = \phi\,(T, P, m_1, \ldots, m_k, \ldots, m_m) \tag{18}$$

The differential of $\underline{H}_g$ can be expressed as :

$$d\underline{H}_g = \left(\frac{\partial \underline{H}_g}{\partial T}\right)_{P,m} dT + \left(\frac{\partial \underline{H}_g}{\partial P}\right)_{T,m} dP + \sum_{k=1}^{\tilde{m}} \left(\frac{\partial \underline{H}_g}{\partial m_{k,g}}\right)_{P,T,m_{i,g}} dm_{k,g}$$

$$= m_g C_{P,g}\,dT + \left\{ \underline{V}_g - m_g T \left(\frac{\partial V_g}{\partial T}\right)_{P,y} \right\} dP + \sum_{k=1}^{\tilde{m}} \bar{H}_{k,g}\,dm_{k,g} \tag{19}$$

Similarly

$$d\underline{H}_\ell = m_\ell C_{P,\ell}\,dT + \left\{ \underline{V}_\ell - m_\ell T \left(\frac{\partial V_\ell}{\partial T}\right)_{P,x} \right\} dP + \sum_{k=1}^{\tilde{m}} \bar{H}_{k,\ell}\,dm_{k,\ell} \tag{20}$$

The calorimeter volume $\underline{V}$ is constant :

$$d\underline{V} = d\underline{V}_g + d\underline{V}_\ell = 0 \tag{21}$$

The change in internal energy of the calorimeter can be expressed as :

$$d\underline{E}_c = C_c \, dT \tag{22}$$

where C_c is the heat capacity of the calorimeter.

Combining Equations (11), (13), (14), (16), (17), (19), (20), (21), (22), and (23) and rearranging results in

$$\sum_{k=1}^{n} \bar{H}_{k,g} \, dm_{k,g} + \sum_{k=1}^{n} \bar{H}_{k,\ell} \, dm_{k,\ell}$$

$$+ \left(m_g C_{P,g} + m_\ell C_{P,\ell} + C_c \right) dT$$

$$- \left\{ m_g T \left(\frac{\partial V_g}{\partial T} \right)_{P,y} + m_\ell T \left(\frac{\partial V_\ell}{\partial T} \right)_{P,x} \right\} dP = \underline{q} + \sum_{k=1}^{n} \bar{H}_{k,a} \, dm_{k,a} \tag{23}$$

The left-hand side of this equation represents the changes that take place within the calorimeter. The terms on the right-hand side represent items that can be observed outside the calorimeter.

The terms $dm_{k,l}$ and $dm_{k,g}$ can not be measured experimentally and must be expressed in terms of measurable quantities. The term $dm_{k,l}$ will first be eliminated.

A material balance for any component k can be expressed as

$$dm_{k,\ell} = dm_{k,a} - dm_{k,g} = y_{k,a} \, dm_a - d(y_k m_g) \tag{24}$$

It is convenient to write the term $\bar{H}_{k,a}$ as

$$\bar{H}_{k,a} = \left(\bar{H}_{k,a} - \bar{H}_{k,g} \right) + \bar{H}_{k,g} \tag{25}$$

Substitution of Equations (24) and (25) into Equation (23) yields

$$
\begin{aligned}
\left\{\sum_{k=1}^{\tilde{n}} \left(\bar{H}_{k,g} - \bar{H}_{k,\ell}\right) y_{k,a}\right\} dm_a = \\
&- \left\{\sum_{k=1}^{\tilde{n}} \left(\bar{H}_{k,a} - \bar{H}_{k,g}\right) y_{k,a}\right\} dm_a \\
&+ \sum_{k=1}^{\tilde{n}} \left(\bar{H}_{k,g} - \bar{H}_{k,\ell}\right) d\left(y_k m_g\right) \\
&- \underline{q} + \left(m_g C_{P,g} + m_\ell C_{P,\ell} + C_c\right) dT \\
&- \left\{ m_g T \left(\frac{\partial V_g}{\partial T}\right)_{P,y} + m_\ell T \left(\frac{\partial V_\ell}{\partial T}\right)_{P,x}\right\} dP \qquad (26)
\end{aligned}
$$

This equation represents the relation between the system properties and a number of variables that can be determined experimentally. The equation is rigorous and can be applied to any equilibrium process for addition or withdrawal of gaseous material from an isochoric vessel.

In the case of vaporization it proves to be useful to write the differential $d(y_k\, m_g)$ as

$$d\left(y_k m_g\right) = y_k\, dm_g + m_g\, dy_k \qquad (27)$$

An expression for dm_g can be obtained by utilizing the fact that the calorimeter volume $\underline{V}$ is constant :

$$\underline{V} = m_g V_g + m_\ell V_\ell \qquad (28)$$

$$d\underline{V} = 0 =$$

$$m_g \, dV_g + V_g \, dm_g + m_\ell \, dV_\ell + V_\ell \, dm_\ell \tag{29}$$

Substitution of the overall material balance

$$dm_\ell = dm_a - dm_g \tag{30}$$

results in

$$dm_g = - \left(\frac{m_g \, dV_g + m_\ell \, dV_\ell + V_\ell \, dm_a}{V_g - V_\ell} \right) \tag{31}$$

For vaporization

$$\bar{H}_{k,a} = \bar{H}_{k,g} \tag{32}$$

$$y_{k,a} = y_{k,g} \tag{33}$$

By combining Equations (26), (27), (31), (32), and (33) a general expression for an equilibrium vaporization process is obtained :

$$\left\{ \sum_{k=1}^{n} (\bar{H}_{k,g} - \bar{H}_{k,\ell}) \, y_k \right\} = \left(\frac{V_g - V_\ell}{V_g \, dm_a + m_g \, dV_g + m_\ell \, dV_\ell} \right)$$

$$\Big[m_g \sum_{k=1}^{n} (\bar{H}_{k,g} - \bar{H}_{k,\ell}) \, dy_k - \underline{q}$$

$$+ (m_g C_{P,g} + m_\ell C_{P,\ell} + C_c) \, dT$$

$$- \left\{ m_g T \left(\frac{\partial V_g}{\partial T} \right)_{P,y} + m_\ell T \left(\frac{\partial V_\ell}{\partial T} \right)_{P,x} \right\} dP \Big] \tag{34}$$

The integration of the differential Equations (26) and (34) over the path of some particular processes will now be considered.

Isothermal Vaporization of a One-Component System

In this case all state variables are constant and Equation (34) can be integrated to yield the latent heat of vaporization

$$H_g - H_\ell = \frac{-\underline{Q}}{\Delta m_a}\left(\frac{V_g - V_\ell}{V_g}\right) = Q\left(\frac{V_g - V_\ell}{V_g}\right) \qquad (35)$$

where $\underline{Q}$ is the integral of $\underline{q}$ and Q is the total energy input per unit mass of material withdrawn.

In an actual vaporization process a small amount of liquid superheating occurs. The bulk liquid temperature T_l is slightly higher than the vapor temperature T_g. The magnitude of the superheat encountered in this investigation was of the order of 0.1°F. The actual vaporization takes place at the vapor-liquid interface. The temperature and pressure at the interface can be considered to be the same as in the vapor. The measured quantity $(H_g - H_l)$ may be rewritten as

$$H_g - H_\ell = (H_g)_{T_g} - (H_\ell)_{T_\ell} =$$

$$(H_g - H_\ell)_{T_g} - c_{P,\ell}(T_\ell - T_g) \qquad (36)$$

Thus the latent heat of vaporization at the vapor temperature is equal to

$$(H_g - H_\ell)_{T_g} = Q\left(\frac{V_g - V_\ell}{V_g}\right) - c_{P,\ell}(T_\ell - T_g) \qquad (37)$$

The bulk liquid temperature is known more accurately than the vapor temperature and the liquid temperature is maintained at an integral value of temperature (e.g. 100.00°F). It is therefore advisable to express the final result at the liquid temperature. The effect of temperature on the latent heat of vaporization is given by

$$\frac{d\,(H_g - H_\ell)''}{d\,T} = (C_{P,g} - C_{P,\ell}) + \left[\left\{V_g - T\left(\frac{\partial V_g}{\partial T}\right)_P\right\} - \left\{V_\ell - T\left(\frac{\partial V_\ell}{\partial T}\right)_P\right\}\right]\frac{dP''}{dT} \qquad (38)$$

For small changes in temperature the last term is negligible and the following holds

$$(H_g - H_\ell)_{T_\ell} = (H_g - H_\ell)_{T_\ell} - (C_{P,g} - C_{P,\ell})(T_\ell - T_g) \qquad (39)$$

By combining Equations (39) and (37) the latent heat of vaporization at the bulk liquid temperature is obtained:

$$(H_g - H_\ell)_{T_\ell} = Q\left(\frac{V_g - V_\ell}{V_g}\right) + C_{P,g}(T_\ell - T_g) = \Delta H_v \qquad (40)$$

In order to evaluate ΔH_v it is necessary to know V_g and V_l. If accurate values of dP''/dT can be obtained, it is possible to eliminate the use of V_g by means of the Clapeyron equation :

$$\Delta H_v = (V_g - V_\ell)\ T\ dP''/dT \qquad (41)$$

Equations (40) and (41) can be combined to give

$$\Delta H_v = \left\{ Q + C_{P,g}(T_l - T_g) \right\} - V_l T \frac{dP''}{dT} \left\{ 1 - C_{P,g} \frac{T_l - T_g}{\Delta H_v} \right\} \qquad (42)$$

This is a convenient formula to calculate ΔH_v from experimental data when V_g is not known. The term $C_{P,g}(T_l - T_g)/\Delta H_v$ is usually entirely negligible. By neglecting this term and by substituting the Clapeyron equation into Equation (42) the following expression for the dew-point volume is obtained :

$$V_g = \frac{Q + C_{P,g}(T_l - T_g)}{T \; dP''/dT} \qquad (43)$$

Isothermal Vaporization of a Single Volatile Component for a Multicomponent System

For this case Equation (34) reduces to

$$(H^{\circ}_{k,g} - \bar{H}_{k,l}) = \left(\frac{V_g - V_l}{V_g \, dm_a + m_g \, dV_g + m_l \, dV_l} \right) \left[-\underline{q} - \left\{ m_g T \left(\frac{\partial V_g}{\partial T} \right)_{P,y} + m_l T \left(\frac{\partial V_l}{\partial T} \right)_{P,x} \right\} dP \right] \qquad (44)$$

If only a few per cent of the calorimeter contents are withdrawn during a test, the variation in $(H^{\circ}_{k,g} - \bar{H}_{k,l})$ will be small. Similarly the variation of all state properties will be small and average values (designated as *) may be used in the integration of Equation (44) :

$$(H^{\circ}_{k,g} - \bar{H}_{k,l})^{*} = \left(\frac{V_g^{*} - V_l^{*}}{V_g^{*} \Delta m_a + m_g^{*} \Delta V_g + m_l^{*} \Delta V_l} \right) \left[- \underline{Q} - \left\{ m_g T \left(\frac{\partial V_g}{\partial T} \right)_{P,y} + m_l T \left(\frac{\partial V_l}{\partial T} \right)_{P,x} \right\}^{*} \Delta P \right] \qquad (45)$$

$(H^{o}_{k,g}-\bar{H}_{k,1})$ may be corrected again for superheat by adding the correction term :

$$(H^{\circ}_{k,g} - \bar{H}_{k,l})^{*}_{T_l} = (H^{\circ}_{k,g} - \bar{H}_{k,l})^{*} + C_{P,g}(T_l - T_g)^{*} \qquad (46)$$

In cases where V_g and m_g change appreciably over a run the use of Equation (45) can introduce small errors. A better equation can be obtained by applying Equation (26) to this case in the form

$$(H^{\circ}_{k,g} - \bar{H}_{k,l})^{*} = \left(\frac{1}{\Delta m_a - \Delta m_g} \right) \left[- \underline{Q} - \left\{ m_g T \left(\frac{\partial V_g}{\partial T} \right)_{P,y} + m_l T \left(\frac{\partial V_l}{\partial T} \right)_{P,x} \right\}^{*} \Delta P \right] \qquad (47)$$

where Δm_g can be calculated from

$$\Delta m_g = \Delta \left(\frac{\underline{V} - \underline{m} V_l}{V_g - V_l} \right) \qquad (48)$$

This is the recommended final equation. Equation (45) has been included because it points out very clearly the differences between the equation for a mixture and the equation for a pure component, i.e. Equation (35).

Isothermal Vaporization of a Binary System

The integral form of Equation (34) for this case may be written as

$$\left\{ \sum_{k=1}^{2} (\bar{H}_{k,g} - \bar{H}_{k,l})\, y_k \right\}^{*} = \left\{ \frac{V_g^{*} - V_l^{*}}{V_g^{*}\, \Delta m_a} + \frac{V_g^{*} - V_l^{*}}{m_g^{*}\, \Delta V_g + m_l^{*}\, \Delta V_l} \right\} \left[-\underline{Q} - \left\{ m_g T \left(\frac{\partial V_g}{\partial T}\right)_{P,y} + m_l T \left(\frac{\partial V_l}{\partial T}\right)_{P,x} \right\}^{*} \Delta P + m_g^{*} \sum_{k=1}^{2} (\bar{H}_{k,g} - \bar{H}_{k,l})^{*}\, \Delta y_k \right] \tag{49}$$

Comparison with Equation (45) shows that there is one additional term in Equation (49) to account for the change in vapor composition. Otherwise the equations are similar in form. A better equation can again be obtained from Equation (26) :

$$\left\{ \sum_{k=1}^{2} (\bar{H}_{k,g} - \bar{H}_{k,l})\, y_k \right\}^{*} \Delta m_a = \sum_{k=1}^{2} (\bar{H}_{k,g} - \bar{H}_{k,l})^{*}\, \Delta(y_k\, m_g) - \underline{Q} - \left\{ m_g T \left(\frac{\partial V_g}{\partial T}\right)_{P,y} + m_l T \left(\frac{\partial V_l}{\partial T}\right)_{P,x} \right\}^{*} \Delta P \tag{50}$$

The material corresponding to the increase in vapor phase does not have the composition y_k^* but is slightly richer in component j. This is a consequence of the increase in the weight fraction of the heavy component j during the test. With this in mind the following rearrangement can be made

$$\sum_{k=1}^{2} (\bar{H}_{k,g} - \bar{H}_{k,\ell})\, \Delta m_{k,g} =$$

$$\frac{\Delta m_{k,g}}{y_k} \left\{ (\bar{H}_{k,g} - \bar{H}_{k,\ell})\, y_k + (\bar{H}_{j,g} - \bar{H}_{j,\ell})\, y_j \right\}$$

$$+ (\bar{H}_{j,g} - \bar{H}_{j,\ell}) \left\{ \Delta m_{j,g} - \left(\frac{1 - y_k}{y_k} \right) \Delta m_{k,g} \right\} \qquad (51)$$

Substitution into Equation (50) results in

$$\left\{ \sum_{k=1}^{2} (\bar{H}_{k,g} - \bar{H}_{k,\ell})\, y_k \right\}^* =$$

$$\left\{ \frac{1}{\Delta m - \Delta m_{k,g} / y_k} \right\}$$

$$\left[-\underline{Q} - \left\{ m_g T \left(\frac{\partial V_g}{\partial T} \right)_{P,y} + m_\ell T \left(\frac{\partial V_\ell}{\partial T} \right)_{P,x} \right\}^* \Delta P \right.$$

$$\left. + (\bar{H}_{j,g} - \bar{H}_{j,\ell})^* \left\{ \Delta m_{j,g} - \left(\frac{1 - y_k}{y_k} \right) \Delta m_{k,g} \right\} \right] \qquad (52)$$

The last term reflects the change in vapor composition during the test. The quantities $\Delta m_{k,g}$ and $\Delta m_{j,g}$ can be calculated from

$$\Delta m_{k,g} = \Delta \left\{ y_k \left(\frac{\underline{V} - \underline{m} \, V_\ell}{V_g - V_\ell} \right) \right\} \tag{53}$$

Equations (52) and (53) represent the final recommended relations to be used in the calculations. The meaning of the various terms will now be considered.

The quantity $\sum_{k=1}^{2} (\bar{H}_{k,g} - \bar{H}_{k,1}) y_k$ represents the enthalpy change upon vaporization per unit weight of vapor formed at the average liquid composition of the test. It is the result to be calculated from the experimental data.

The term Δm represents the weight of material withdrawn, or more properly, the increase in weight of the system. It is thus negative and has the composition y_k^*, i.e. the vapor composition corresponding to the average liquid composition during the test. Some additional material of composition y_k^* was vaporized that stayed within the calorimeter. This quantity is equal to $(\Delta m_{k,g}/y_k)$. The second term of Equation (51) therefore represents the reciprocal of the total amount of material of composition y_k^* that was vaporized. In addition some pure component j was vaporized to change the vapor composition during the test. The last term of Equation (52) represents that amount of component j, multiplied by its partial enthalpy change upon vaporization.

The term *Q* represents the total amount of energy added to the system during the test. *Q* consists of energy added electrically, by agitation and by conduction and radiation.

The fourth term of Equation (52) may be written as

$$-\left\{ m_g \, T \left(\frac{\partial V_g}{\partial T}\right)_{P,y} + m_\ell \, T \left(\frac{\partial V_\ell}{\partial T}\right)_{P,x} \right\}^* \Delta P =$$

$$+ \left\{ m_g \, \ell_{P,g} + m_\ell \, \ell_{P,\ell} \right\}^* \Delta P = \underline{\ell}_P^{\,*} \, \Delta P \tag{54}$$

where l_p is the latent heat of pressure change. The latter property is normally negative and since Δ P is negative it follows that the fourth term of Equation (52) is positive.

The details of the application of Equations (52) and (53) to the n-butane-n-decane system are given under Calculations.

Adiabatic Addition of a Pure Component to a Multicomponent System

This method can be used to measure the partial enthalpy change upon condensation of a component for a system with several volatile components. In this process condensation takes place and the temperature and pressure rise. The integral form of Equation (26) becomes

$$
\begin{aligned}
(\bar{\ }_{g} - \bar{H}_{k,\ell})^{*} \Delta m_{k,a} = & -(H^{\circ}_{k,a} - \bar{H}_{k,g})^{*} \Delta m_{k,a} \\
& + \sum_{k=1}^{n} (\bar{H}_{k,g} - \bar{H}_{k,\ell}) \Delta (y_k m_g) \\
& - (\underline{Q}_s + \underline{Q}_{c+r}) + (m_g C_{P,g} + m_\ell C_{P,\ell} + C_c)^{*} \Delta T \\
& - \left\{ m_g T \left(\frac{\partial V_g}{\partial T}\right)_{P,y} + m_\ell T \left(\frac{\partial V_\ell}{\partial T}\right)_{P,x} \right\}^{*} \Delta P \qquad (55)
\end{aligned}
$$

The Δ T term is the significant one here and the heat capacity of the system must be known accurately. The heat capacity can be measured before and after an addition run and an average value can be used for the evaluation of the results of the addition run.

During a heat capacity run electrical energy is put into the system but no material is added. Equation (55) then becomes

$$
\begin{aligned}
\underline{Q} = & \sum_{k=1}^{n} (\bar{H}_{k,g} - \bar{H}_{k,\ell})^{*} \Delta (y_k m_g) \\
& + \Big[(m_g C_{P,g} + m_\ell C_{P,\ell} + C_c) \\
& - \left\{ m_g T \left(\frac{\partial V_g}{\partial T}\right)_{P,y} + m_\ell T \left(\frac{\partial V_\ell}{\partial T}\right)_{P,x} \right\} \frac{dP''}{dT} \Big]^{*} \Delta T \qquad (56)
\end{aligned}
$$

The second term can be safely estimated using approximate values for the partial enthalpy changes, since this term is small compared to $\underline{Q}$. The coefficient of the ΔT term can be considered as an effective total heat capacity C_T :

$$c_T = \Big[\left(m_g C_{P,g} + m_\ell C_{P,\ell} + C_c \right) - \Big\{ m_g T \left(\frac{\partial V_g}{\partial T} \right)_{P,y} + m_\ell T \left(\frac{\partial V_\ell}{\partial T} \right)_{P,x} \Big\} \frac{dP''}{dT} \Big] \qquad (57)$$

C_T can be measured before and after a run and the average value C_T^* can be used for the addition run. Equation (55) then reduces to

$$\left(\bar{H}_{k,g} - \bar{H}_{k,\ell} \right)^* \Delta m_{k,a} = - \left(H^{\circ}_{k,a} - \bar{H}_{k,g} \right) \Delta m_{k,a} + \sum_{k=1}^{\sim} \left(\bar{H}_{k,g} - \bar{H}_{k,\ell} \right)^* \Delta \left(y_k m_g \right) - \left(\underline{Q}_s + \underline{Q}_{c+r} \right) + c_T^* \Delta T \qquad (58)$$

During the condensation process the temperature, the pressure and the composition of the system all change. The significant change is the change in temperature since it determines the final result. In addition to the condensation of the component k added to the system, small quantities of other volatile components will also condense. This is reflected in the third term of Equation (58).

The second term can be written as

$$(H^{\circ}_{k,a} - \bar{H}_{k,g}) = (H^{\circ}_{k,a} - \bar{H}_{k,g})_T + (T_a - T)\, C^{\circ}_{p,k} \qquad (59)$$

since the temperature T_a of the entering gas is not necessarily the same as the system temperature T. If it is assumed that there is no heat of mixing on addition of pure component k to the system vapor, then $(H^{o}_{k,a} - \bar{H}_{k,g})_T = 0$. In any case it can be expected to be very small compared to $(\bar{H}_{k,g} - \bar{H}_{k,l})$. Equation (59) then enables the evaluation of the change in partial enthalpy of component k upon condensation (or vaporization). It will be an average value over the changes in temperature and composition that take place during the run.

APPARATUS

In principle, the experimental procedure consists of adding a measured amount of electrical energy to a calorimeter containing coexisting liquid and gas phases of the system being studied, and collecting the vaporized material in a chilled weighing bomb.

The calorimeter is shown schematically in Figure 2 and consists of a spherical stainless steel vessel A which is supported by means of fine wires within a vacuum jacket. The vacuum jacket is surrounded by an oil bath B and the oil-bath temperature is automatically controlled at a constant value by means of a thyratron control circuit. The calorimeter is loaded and unloaded through a connection in the bottom. The liquid within the calorimeter is circulated by means of a centrifugal agitator C. The liquid flows past an electrical heater D, around and through ports in the shield E, and past a thermometer well F containing a platinum resistance thermometer in a helium atmosphere. The addition of energy by the heater vaporizes the sample and the vapor is withdrawn at the top of the calorimeter through a small tube H and passes through an orifice I into a weighing bomb J or K. The orifice diameter is sufficiently small to obtain sonic flow through the orifice. Condensation in the withdrawal line H is prevented by maintaining the line at a temperature slightly above the calorimeter temperature.

The oil bath temperature is measured with a platinum resistance thermometer and this thermometer is used as the absolute temperature reference. The equality of the temperature of the calorimeter and the oil bath is established by means of two copper-constantan differential thermocouples. The pressure within the vacuum jacket is maintained below 10^{-8} inch of mercury by means of an oil diffusion pump L and a mechanical forepump M. A separate vacuum system consisting of a mercury diffusion pump and a mechanical forepump is used to evacuate the calorimeter and the loading and withdrawal lines. The oil bath and calorimeter temperatures are measured with Mueller bridges. A White potentiometer is used to measure the E.M.F. of fourteen thermocouples. Electrical heaters maintain the equipment at the required temperature. A Rubicon potentiometer is used to measure the current to and the voltage across the calorimeter heater.

Figure 3 shows the general arrangement of the equipment. It is drawn to scale and the overall height of the equipment shown is approximately six feet. The main features to be noted are the calorimeter bomb A, the vacuum jacket J, and the oil bath K. Circulation within the oil bath is provided by impeller L. The impeller is driven by pulley B' through sleeves V and W. The tube H is an extension of the calorimeter bomb A and encloses the drive shaft G for the calorimeter agitator B. Shaft G is connected to the armature H'. Torque for turning the agitator is transmitted to the armature H' by means of the rotating electromagnets K'. The electromagnet assembly is driven by the pulley P'. The material was added to the calorimeter through a tube (not shown) entering the lower end of tube H at point E'. The equipment described above was used earlier to measure latent heats of vaporization of pure substances (see Part I and II). A detailed description of the apparatus is available (1, 13). The equipment was modified for this project to enable measurement of the pressure within the calorimeter. As indicated in Figure 2, the pressure within the calorimeter is transmitted through a metal diaphragm N to the pressure measuring device G.

Diaphragm

The diaphragm block is shown in detail in Figure 4. The diaphragm A is two inches in diameter and 0.020 inch thick and is part of the stainless steel cylinder B. The cavity under the diaphragm is connected to the calorimeter through the fitting C of Figure 4 and the tube H of Figure 3. The space above the diaphragm was filled with mercury to just below the pointed lower end of the level indicator F. The space above the mercury was filled with hydraulic oil and was connected to a dead weight pressure gauge tester. The level indicator F is electrically insulated by means of the Bakelite rings H and K. An E.M.F. of 120 volt was established between the level indicator and the mercury by means of an electrical circuit consisting of four 30 volt D.C. batteries in series, a 4.7 meg ohm resistor and a 0.04 watt neon light. The neon light was shunted with a 15 meg ohm resistor.

When the pressure in the calorimeter increases, the diaphragm is stressed and moves upward. The mercury level rises and makes contact with the level indicator as shown by the neon light. The diaphragm can be returned to its zero position by increasing the oil pressure until the light goes off. At this point the calorimeter pressure is balanced by the known oil pressure. A small movement of the two-inch diameter diaphragm produces a magnified movement of the mercury level since the mercury column has a diameter of only 1/8 inch. The tip of the indicator F has a diameter of 0.015 inch. The maximum upward movement of the diaphragm is limited by a backing plate. This is a protection against non-elastic deformation at high calorimeter pressures.

Some trouble was encountered in completely filling the narrow space between the diaphragm and the backing plate with mercury, although the mercury was added under high vacuum conditions. This was overcome by drilling a small horizontal hole (not shown) through the shell B to the space between the diaphragm and the backing plate. A fitting with a valve (also not shown) connected the hole to a variable height mercury reservoir. This made it possible to add the mercury at the lowest point and solved the earlier difficulties. It also had the advantage of enabling the mercury level to be adjusted during calibration without having to remove the oil above the mercury.

The mercury was contained by the copper seal rings D. These were compressed by tightening the large nut L. Initially some mercury leakage was encountered under high pressure; this was eliminated by providing L with twelve evenly spaced set-screws (not shown). By tightening the set-screws the nut L, together with the inner cylinder I, moves upward with respect to the fitting M and thus compresses the copper rings D. In this way a more even pressure distribution along the copper rings was obtained than was previously possible.

Ashcroft Gauge Tester

A dead weight pressure gauge tester was used to apply a known pressure to the diaphragm. The particular instrument employed was an Ashcroft #1300 gauge tester with a capacity of 500 psi and an accuracy of 0.1 psi. In principle, the instrument consists of a piston rotating inside a cylinder filled with oil. By putting appropriate weights on the piston platform, a known pressure is produced in the oil under the piston. The piston is rotated during a measurement to minimize friction effects. The weights (P_w) must be multiplied by a factor A to obtain psi.

The instrument was calibrated against the No.1 pressure balance of the Chemical Engineeering Laboratory. The results are shown in Figure 5. None of the points of Figure 5 deviates more than 0.04 psi from the straight line. The calibration constant A increases slightly with the load.

Calibration

The diaphragm is said to be in its zero position when the indicator light is in the on-off position. The zero position can be changed by changing the amount of mercury above the diaphragm. The best position was found to be at a mercury setting where the oil pressure was approximately 12 psi less than the calorimeter pressure. The optimum position did not occur at the zero position as one might expect. McKay (1) already reported that the diaphragm was stretched. Examination of the diaphragm showed a permanent deformation toward the calorimeter side, i.e. the side without the backing plate. This probably accounts for the above behavior.

The pressure in the calorimeter is related to the instrument variables by

$$P = A P_w + B + P_{atm} - 0.030/V_l \qquad (60)$$

A = calibration constant of gauge tester

P_w = load in weights, psi

B = additive constant to allow for the zero position diaphragm tension, the weight of the piston, and the hydrostatic head of oil and mercury between the piston and the diaphragm, psi

P_{atm} = atmospheric pressure acting on piston, psi

$.030/V_1$ = term to account for 4.3 ft of calorimeter fluid, psi, with V_1 in cu ft/lb

The constant B was determined by calibration against the known vapor pressure of trans-2-butene. Seven calibrations at different temperatures over the pressure range of 80-330 psia yielded and average value for B of 17.4 psi. The average deviation from the above value was 0.5 psi. The deviations were random with respect to pressure. When the gauge tester was balanced, a change of 0.1 or 0.2 psi in weights would turn the indicator light on or off. However, when all the weights were removed from the piston and then put back again, the balancing load might be 0.5 psi different from the earlier.one. From this behavior it was concluded that the condition of the diaphragm was limiting the accuracy of the pressure measurement to one psia.

Porous Metal Orifice

The vapor withdrawal rate was controlled by an orifice. Eight orifice sizes in the range from 0.0014 to 0.198 inch in diameter were available. At the high pressures encountered in this investigation a smaller orifice was required to obtain low enough flow rates. It is difficult to make a very small orifice of a prescribed size. A flow restrictor was made using a 0.070 inch thick disc of 25 SS (2-5 microns) Crespor porous Monel supplied by the Asco Sintering Corporation of Los Angeles. A circular area with a diameter of 0.015 inch gave a withdrawal rate equivalent to a 0.0009 inch conventional orifice. The porous metal orifice was relatively easy to make and performed satisfactorily.

MATERIALS

The n-butane employed in this investigation was obtained from the Phillips Petroleum Company as research grade material with a reported purity of 99.94 mole per cent, as indicated by its freezing point. The most probable impurity was iso-butane. A sample of the material was passed through a bed of Drierite (anhydrous calcium sulphate) to remove any traces of water. Any dissolved air was removed by freezing the material, using liquid nitrogen as the refrigerant, and subsequent evacuation. The material was brought to the liquid state again by warming it to room temperature. The deaeration operation was repeated until a constant pressure was observed above the frozen material in two successive operations. It was found that the vapor pressure of the sample changed 0.21 psi with a change in quality from 0.1 to 0.8 at 100°F.

The n-decane used in this investigation was also obtained from the Phillips Petroleum Company as research grade. It was reported to contain 99.49 mole per cent n-decane, based on determinations of the freezing point. The most probable impurities were other normal paraffins and isoparaffins in the same boiling range. The n-decane sample showed an index of refraction of 1.40963 relative to the D-line of sodium at 77°F , as compared with a value of 1.40967 reported by A.P.I. Research Project 44 (14) for an air-saturated sample at the same temperature. At 77°F , the specific weight was 45.338 pounds per cubic foot, as compared with the reported value

(14) of 45.337 pounds per cubic foot.

From the result of these measurements it was concluded that the n-butane and n-decane samples met the purity standards for this investigation. Uncertainty in the results due to impurities is believed to be negligible relative to the experimental uncertainties.

EXPERIMENTAL PROCEDURES

Transfer of Materials into Calorimeter

The n-decane was dried over freshly extruded sodium and transferred to an evacuated weighing bomb. The material was deaerated as follows : The bomb was chilled with liquid nitrogen to freeze the n-decane and then evacuated. After bringing the bomb contents to the liquid state by heating to room temperature, the bomb was again chilled and any remaining air pumped off. The bomb was weighed and the n-decane was distilled into the evacuated calorimeter by heating the weighing bomb by means of an oil bath. After the transfer the n-decane in the lines was collected inthe weighing bomb by chilling the bomb with liquid nitrogen. A final weighing established the amount of material transferred to the calorimeter.

The n-butane transfer was very similar. The gas was dried by passing it through a bed of fresh Drierite (anhydrous calcium sulphate); it was then condensed in a chilled weighing bomb and deaerated. A boiling water bath was used to heat the bomb during the distillation process.

Throughout the investigation an accurate account was kept of the amount of material remaining in the calorimeter and additions were made when necessary. The liquid level must be maintained between 685 cc at room temperature and 1160 cc at the operating temperature.

These figures correspond to 53 per cent and 90 per cent respectively of the calorimeter volume of 1292 cc. The lower limit corresponds to the minimum liquid volume required to cover the heater. The upper limit insures that the total liquid volume never approaches the calorimeter volume and also minimizes any entrainment during vaporization.

Preliminary Operations

The oil bath and the calorimeter were brought to the operating temperature and the oil bath was put on automatic control by means of a thyratron control circuit. The temperature gradient along each of the two tubes leading from the top of the calorimeter was reduced to nearly zero by adjustment of the appropriate guard heaters. The temperature of the vapor withdrawal lines from the vacuum jacket to the vapor receiving block was adjusted to approximately 5°F above the calorimeter temperature. Two tared weighing bombs were attached to the vapor receiving block and cooled with liquid nitrogen. One was an 80 cc evacuated bomb to receive the sample and the other was a 700 cc bomb containing material from previous runs. The vapor line from the orifice block to the weighing bombs was evacuated. In addition the vacuum between the calorimeter and the oil bath, maintained by a separate vacuum system, was checked. When the calorimeter was exactly at the oil-bath temperature, as indicated by a differential thermocouple, the calorimeter temperature was recorded. This temperature represents the optimum starting condition for a run. At this stage the calorimeter heater was turned on. The vapor flow was started by opening the valve to the large weighing bomb and one or more orifice valves. The electrical energy input was adjusted until the temperature of the calorimeter was nearly constant and very close to that of the oil bath.

Test Run

When the calorimeter temperature was exactly at the optimum starting temperature, the vapor flow was diverted from the large bomb to the small bomb and a timer was started at the same time. The starting pressure was recorded and periodic readings were taken of the calorimeter pressure and temperature, and the current to and the voltage across the calorimeter heater. In addition, the oil bath control setting was adjusted when required and the readings of the ten thermocouples along the vapor withdrawal path were recorded. The temperature difference between the liquid phase and the outgoing gas within the calorimeter bomb was measured to determine superheat effects. During the run the pressure dropped and this reduced the vapor withdrawal rate. Consequently, the temperature tended to increase and minor adjustments to the heater current were made at recorded integral times. The calorimeter temperature variations were kept to within 0.005°F. Two operators were required to take all the instrument readings during a run. After 10-20 grams of vapor were withdrawn the run was stopped when the calorimeter temperature was exactly equal to the starting temperature. The final pressure was measured and the vapor in the withdrawal lines was collected in the larger bomb.

The weight of material withdrawn during the pre-run and the sample weight were determined from the final weights of the large and small bombs.respectively. The contents of the small bomb were quantitatively transferred to the large bomb so that all the material leaving the calorimeter was collected in the large bomb. The original mixture in the calorimeter could thus be reproduced when necessary.

Agitator Calibration

The rate of agitator input was determined by measuring the rate of temperature rise of the system when only the agitator was on and when some electrical energy was supplied as well. The oil bath temperature was adjusted frequently during these processes to maintain zero temperature difference between the oil bath and the calorimeter.

CALCULATIONS

The enthalpy change upon vaporization was computed from the experimental data by means of Equation (52) :

$$\left\{\sum_{k=1}^{2}(\bar{H}_{k,g}-\bar{H}_{k,\ell})\,y_k\right\}^* = \left\{\frac{1}{\Delta m - \Delta m_{k,g}/y_k}\right\}$$

$$\left[-\underline{Q} - \left\{m_g T\left(\frac{\partial V_g}{\partial T}\right)_{P,y} + m_\ell T\left(\frac{\partial V_\ell}{\partial T}\right)_{P,x}\right\}^* \Delta P\right.$$

$$\left. + (\bar{H}_{j,g}-\bar{H}_{j,\ell})^* \left\{\Delta m_{j,g} - \left(\frac{1-y_k}{y_k}\right)\Delta m_{k,g}\right\}\right] \qquad (61)$$

Since the n-decane (component j) is only slightly volatile, this equation can be rearranged to yield an expression for the partial enthalpy change upon vaporization for the n-butane (component k) :

$$(\bar{H}_{k,g}-\bar{H}_{k,\ell})^* = \left\{\frac{1}{y_k^*\,\Delta m - \Delta m_{k,g}}\right\}$$

$$\left[-\underline{Q} - \left\{m_g T\left(\frac{\partial V_g}{\partial T}\right)_{P,y} + m_\ell T\left(\frac{\partial V_\ell}{\partial T}\right)_{P,x}\right\}^* \Delta P\right.$$

$$\left. + (\bar{H}_{j,g}-\bar{H}_{j,\ell})^* \left\{\Delta m_{j,g} - y_j\,\Delta m\right\}\right] \qquad (62)$$

It should be noted that Δm and ΔP are negative quantities; $\Delta m_{k,g}$ and $\Delta m_{j,g}$ are nearly always positive.

Weight of Material Vaporized

In addition to the material Δm withdrawn from the calorimeter, some material was vaporized that stayed within the calorimeter. The increase in weight of component k in the vapor phase ($\Delta m_{k,g}$) was computed from

$$\Delta m_{k,g} = \Delta \left\{ y_k \left(\frac{\underline{V} - \underline{m}\, V_l}{V_g - V_l} \right) \right\} \qquad (63)$$

$\underline{V}$ represents the known calorimeter volume (1292 cc) and $\underline{m}$ represents the total amount of material within the calorimeter. The latter was known from the initial charge and subsequent withdrawal weights. The compositions y_k and x_k of a binary two-phase system can be established from the pressure and temperature and the P-T-composition relation. The latter information was available (15), as well as the volumetric behavior of the liquid phase (16). Data on the vapor phase specific volume were limited to values calculated from volumetric measurements in the two-phase region (15) at 220°, 280°, and 340°F. At the lower temperatures the vapor is practically all n-butane (see Figure 9).

The compressibility factor of pure n-butane (17) at the pressure and temperature of the binary system was used to compute V_g at 100° and 160° F. The pressure measurement was accurate to about one psia. The pressure was also evaluated from a material balance for the calorimeter and the P-T-composition relations. By assuming a pressure the liquid composition could be computed. If the corresponding vapor pressure did not agree with the assumed pressure, a new pressure was assumed and the procedure repeated until agreement was obtained to within 0.1 psia. The pressure values obtained this way were usually within the accuracy range of the measured pressures. However, the pressures evaluated from the material balance were more consistent and were considered to be more accurate. Consequently the pressures based on the material balance are reported in Table I and these values were used to establish y_k, x_k, V_g, and V_1.

Heat Input Q

The total heat input Q consists of three terms :

$$\underline{Q} = Q_e + Q_s + Q_{c+r} \tag{64}$$

The electrical energy input $\underline{Q}_e$ was computed from the current, voltage, and time measurements. The stirrer energy input Q_s was calculated as

$$Q_s = \left(\frac{S_1}{S_2 - S_1} \right) \left(dQ_{e,s} / d\theta \right) \Delta \theta \tag{65}$$

where

S_1 = rate of temperature rise when only the stirrer is on

S_2 = rate of temperature rise when electrical energy is supplied as well at a rate of $(dQ_{e,s}/d\theta)$.

The energy transferred by conduction and radiation was evaluated from

$$Q_{c+r} = k_T \int_0^{\Delta\theta} (T_{cal} - T_{oil})\, d\theta \tag{66}$$

This formula is not in general agreement with Stefan's law for energy transfer by radiation but is reasonable for small temperature differences. The constants k_T were determined earlier by McKay (1). The evaluation of Q is the same as for a one-component system and has been described in detail (1) (2).

Pressure Drop Heat Effect

The latent heat of pressure change

$$\ell_P = - T \left(\partial V / \partial T \right)_{P,m} \tag{67}$$

for the liquid phase was determined from the volumetric data (16). The results are shown in Figure 6. This data was not available for the gas phase. From the equation of state $P V_g = z b T$ it follows that

$$\left(\partial V_g / \partial T \right)_{P,y} = \frac{b}{P} \left\{ z + T \left(\frac{\partial z}{\partial T} \right)_{P,y} \right\} \tag{68}$$

The compressibility factor z at dewpoint has been discussed on page 87. The term $T\ (\partial z/\partial T)_{P,y}$ is usually only about one-fifth of z and the value of $T(\partial z/\partial T)_{P,y}$ for pure n-butane at the pressure and temperature of the binary system was used. This only introduced negligible errors since the contribution of the total ΔP term is very small. The results are shown in Figure 7. The m_l and m_g values were calculated from

$$m_\ell = \underline{m} - m_g \tag{69}$$

$$m_g = \frac{\underline{V} - \underline{m}\, V_\ell}{V_g - V_\ell} \tag{70}$$

Partial Enthalpy Change upon Vaporization for n-Decane

This property was estimated as

$$(\bar{H}_{j,g} - \bar{H}_{j,\ell}) = \Delta E^{\circ}_{v,j,T} + P(\bar{V}_{j,g} - \bar{V}_{j,\ell}) \tag{71}$$

with

$$\bar{V}_{j,g} = z\, b_j\, T / P \tag{72}$$

The first equation assumes that the internal energy change upon vaporization of n-decane is independent of composition and can thus be taken as the value for the pure component at the same temperature. Figure 14 shows that this is a good assumption for n-butane at temperatures well below its critical temperature of 306°F. This condition is satisfied for n-decane since its critical temperature is 654°F. The vapor phase partial volume was estimated using the compressibility factor z of the binary dew-point vapor. The compressibility factor of the pure component could not be used since n-decane at the pressure and temperature of the system is in the liquid state. The liquid phase partial volume is available (18).

The estimated partial enthalpy changes are included in Table I. It should be noted that a relatively large error in $(\bar{H}_{j,g} - \bar{H}_{j,l})$ will only introduce a small error in $(\bar{H}_{k,g} - \bar{H}_{k,l})$ on account of the low volatility of the n-decane. For instance, even for a n-butane vapor composition of $y_k = 0.90$, a ten per cent error in $(\bar{H}_{j,g} - \bar{H}_{j,l})$ will only introduce one per cent error in $(\bar{H}_{k,g} - \bar{H}_{k,l})$.

RESULTS

The enthalpy change upon vaporization $\sum(\bar{H}_{k,g} - \bar{H}_{k,l})\, y_k$ is shown in Figure 8 as a function of the liquid composition x. The latent heats of vaporization of the pure components form the end points of the isotherms. At 340°F the n-butane is above its critical temperature of 306°F. The critical composition for the n-butane-n-decane system at 340°F occurs at a composition of 0.9 weight fraction n-butane (see Figure 9). The 340°F isotherm thus ends at $x = 0.9$ and $\sum(\bar{H}_{k,g} - \bar{H}_{k,l})\, y_k = 0$. If the 340°F isotherm is linearly extended, it will intercept the critical composition at 34 Btu/lb instead of zero Btu/lb. Thus the 340°F isotherm must curve sharply downward as the critical composition is approached. Steep curves are rather common near the critical point. The root mean square deviation of the experimental points from the smoothed data for Figure 8 is 0.35 Btu/lb. Figure 9 represents the vapor-liquid composition diagram. It is apparent that the vapor consists almost entirely of n-butane except at the higher temperatures. This is well demonstrated in Figure 10 which shows the enthalpy change upon vaporization as a function of the vapor composition. The dotted lines represent an expression for the enthalpy change upon vaporization in which the latent heats of vaporization of the pure components at the same temperature are substituted for the partial enthalpy changes upon vaporization. The difference between the solid and dotted lines of Figure 10 is plotted versus liquid composition in

Figure 11. The lines for each temperature go through zero at liquid compositions corresponding to pure n-decane and pure n-butane. The ordinate of Figure 11 can be considered to be a residual enthalpy change upon vaporization, using as a reference the relation $\sum \Delta \bar{H}^{o}_{v,k} y_k$. It is seen that the residual values are small at 100°F but become larger as the critical temperature of n-butane is approached.

Fractionation is a good example of an industrial process where the results of this investigation are of considerable interest. The pressure in a fractionating column is nearly constant and it is convenient to have a plot of the pertinent data at the particular operating pressure. The enthalpy change upon vaporization at 25 psia has been plotted in Figure 12 as a function of liquid composition x. The points at $x = 0$ and $x = 1$ correspond to the latent heat of vaporization of n-decane and n-butane respectively. The vapor composition is also presented in Figure 12. For steady state conditions Figure 12 shows the heat required to vaporize unit weight of material and the composition of that vapor for a given liquid composition (or tray temperature). The dotted line represents the reference relation $\sum \Delta \bar{H}^{o}_{v,k} y_k$ which is often used in industry to compute heat loads for vaporization processes. It is apparent that at higher temperatures this can lead to significant errors. It should be noted that for heat load calculations it is not necessary to know the individual partial enthalpy changes of the components; a knowledge of the enthalpy change for the system is sufficient. The results so far have demonstrated the various plots that are of interest in a binary system with two volatile components. As mentioned earlier, the n-butane-n-decane system has virtually only one volatile component and this made it possible to evaluate the partial enthalpy change upon vaporization for n-butane.

For an understanding of the behavior of solutions the partial enthalpy change upon vaporization for a component is of primary importance. Figure 13 shows the partial enthalpy change upon vaporization for n-butane as a function of liquid composition at different temperatures. The points at unit weight fraction of n-butane represent the latent heat of vaporization of pure n-butane. Comparison with Figure 8 shows that at zero weight fraction n-butane in the liquid, i.e. at infinite dilution, the partial enthalpy change upon vaporization for n-butane is practically equal to the latent heat of vaporization of n-decane. This is rather surprising but it only holds when the results are expressed on a unit weight basis. On a molar basis this would not be true at all. The results of Figure 13 have been cross-plotted for lines of constant liquid composition in Figure 14. The line $x = 1$ represents the latent heat of vaporization of n-butane as a function of temperature. The critical temperature of n-butane is 306°F. The line for $x = 1.0$ therefore goes to zero at 306°F. The line $x = 0.0$ represents the partial enthalpy change upon vaporization for n-butane.at infinite dilution. The constant composition lines will go to zero at the critical temperatures for the respective compositions. The line $x = 0$ will therefore go to zero at the critical temperature of n-decane, i.e. at 654°F. One can expect that the shape of the constant composition lines is similar to the shape of the line for the latent heat of vaporization of n-butane. The difference between the partial enthalpy change and the latent heat of vaporization is fairly small at 100°F but it becomes greater as the critical temperature of n-butane is approached. Therefore one might expect that the partial enthalpy change upon vaporization of a component is close to the latent heat of vaporization of that component, provided the reduced temperature is reasonably small. The reduced temperature of n-butane at 100°F is equal to 0.73, while the reduced temperature of n-decane at 340°F is 0.70. Assuming corresponding state behavior it appears that up to 340°F the partial enthalpy change for n-decane will be close to its latent heat of vaporization. This observation justifies the use of Equation 71 for estimating the partial enthalpy change upon vaporization for n-decane. As the quantity of n-decane in the vapor increases, the potential error in the partial enthalpy change upon vaporization for n-butane increases. Table I shows that for Test 452 at 340°F the energy associated with the vaporization of the n-decane $(\bar{H}_{j,g} - \bar{H}_{j,l})\, y_j$ represented nineteen per cent of the enthalpy change upon vaporization $\Sigma\, (\bar{H}_{k,g} - \bar{H}_{k,l})\, y_k$.

A ten per cent error in $(\bar{H}_{j,g} - \bar{H}_{j,l})$ would result in a two per cent error in $(\bar{H}_{k,g} - \bar{H}_{k,l})$ here. For all the other tests this figure is much lower as shown by the values of $(\bar{H}_{j,g} - \bar{H}_{j,l})\, y_j$ and $\Sigma\,(\bar{H}_{k,g} - \bar{H}_{k,l})\, y_k$ in Table I. It is apparent from Figure 14 that the lines $x = 0$ and $x = 1$ cross over in the vicinity of 76°F. This means that at lower temperatures the partial enthalpy change will become smaller than the latent heat of vaporization. This is a direct consequence of the behavior of the slopes of the isotherms of Figure 13. As the temperature decreases, the slopes become less negative and, at temperatures below 100°F, even positive.

The partial enthalpy change may be written as the sum of the partial internal energy change and the product of the partial volume change and the pressure

$$(\bar{H}_{k,g} - \bar{H}_{k,\ell}) = (\bar{E}_{k,g} - \bar{E}_{k,\ell}) + P(\bar{V}_{k,g} - \bar{V}_{k,\ell}) \quad (73)$$

Tabulated values of the partial enthalpy change and the partial internal energy change upon vaporization are given in Tables II and III respectively. It was assumed that $V^{o}_{k,g} = \bar{V}_{k,g}$.

The partial internal energy change upon vaporization is a measure of the difference in molecular interactions in the vapor and liquid phases. The potential energy of interaction between molecules in the vapor phase is very much smaller than in the liquid phase. The internal energy change upon vaporization is therefore an indication of the magnitude of the molecular attractions in the liquid phase. The potential energy of interaction for a particular molecule is dependent upon the number and nature of its nearest neighbors. Only if the potential energy of interaction of a molecule k in a liquid mixture is the same as in the pure liquid k can one expect the partial internal energy change upon vaporization to be the same as the value for the pure substance.

The estimated uncertainties of measurement associated with the investigation of the enthalpy change upon vaporization are given in Table IV. These uncertainties vary with the test conditions and the values in Table IV correspond to Test 470 (220°F, $x_k = 0.554$). The energy added by agitation contributes the greatest uncertainty here. As the temperature increases, the uncertainty associated with the dew-point vapor volume becomes the predominant item.

CONCLUSIONS

The enthalpy change upon vaporization (sometimes referred to in the literature as the differential latent heat of vaporization) has been determined for the n-butane-n-decane system over the temperature range 100°- 340°F as a function of composition. The partial enthalpy change upon vaporization for n-butane has been evaluated from these results by applying a correction for the presence of small amounts of n-decane in the vapor. The partial internal energy change upon vaporization for n-butane has also been established. The results are presented in graphical and tabular form. The following conclusioms may be reached for the n-butane-n-decane system :

1. The isotherms for the enthalpy change upon vaporization may be approximated graphically on an enthalpy change-liquid composition diagram by drawing a straight line between the points for the latent heat of vaporization of the pure components at the same temperature, provided the values are expressed on a unit weight basis.
2. This approximation fails at temperatures close to and above the critical temperature of n-butane (306°F).
3. The partial enthalpy change upon vaporization for n-butane increases with decreasing n-butane concentration in the liquid at temperatures above 100°F.

4. At temperatures under 70°F this phenomena appears to reverse itself, i.e. the partial enthalpy change upon vaporization is smaller than the latent heat of vaporization of the pure component.
5. The partial enthalpy change upon vaporization for n-butane at infinite dilution is closely approximated by the latent heat of vaporization of n-decane at the same temperature, provided the results are expressed on a unit weight basis. This is a direct consequence of Conclusion 1.
6. The temperature dependence of the partial enthalpy change upon vaporization at constant liquid composition is similar to the behavior of the latent heat of vaporization of the pure component.

NOMENCLATURE

A	calibration constant of gauge tester
B	additive constant of gauge tester
b	gas constant ft^3, psia/lb $^\circ$R
C_c	heat capacity of calorimeter, Btu/$^\circ$F
C_T	effective total heat capacity, Btu/$^\circ$F
C_P	specific heat capacity at constant pressure; Btu/lb $^\circ$F
E	specific internal energy, Btu/lb
H	specific enthalpy, Btu/lb
k_T	conversion factor, Btu/$^\circ$F, sec
l_P	latent heat of pressure change, Btu/lb
m	weight, lb
n	number of components, weight fraction when used with subscript
P	pressure, lb/in.^{2} absolute, psia
q	infinitesimal quantity of heat transferred to system; Btu/lb
Q	integral of q when used with subscripts, heat transferred to system per unit weight of material withdrawn; Btu/lb
T	absolute temperature; $^\circ$R (degrees Rankine)
V	volume, specific volume, ft^3/lb
w	infinitesimal quantity of work done by system, Btu/lb
x	weight fraction of a component in the liquid phase
y	weight fraction of a component in the vapor phase

z	compressibility factor,,PV/bT
θ	time, seconds

Subscripts

a	relating to the properties of the material added to the system
atm	atmospheric
b	bubble-point liquid
cal	calorimeter
c + r	conduction and radiation
d	dew-point vapor
e	electrical
g	gas phase
j	component j
k	component k
l	liquid phase
oil	oil bath
s	stirrer
v	vaporization

Superscripts

"	two-phase region
-	partial value
o	pure component
*	average value

REFERENCES

1. McKay, R. A., Ph.D. Thesis, Chem. Eng. Dept., Calif. Inst. of Techn., Pasadena, Calif. (1959)
2. Kozicki, William, Ph.D. Thesis, Chem. Eng. Dept., Calif. Inst. of Techn., Pasadena, Calif. (1962)
3. Budenholzer, R. A., Sage, B. H., and Lacey, W. N., Ind. Eng. Chem., 35, 1214 (1943)
4. Burrows, G., J. Appl. Chem., 4, 394 (1954)
5. Hunter, J. B., Bliss, H., Ind. Eng. Chem., 36, 945 (1944)
6. Tyrer, D., J. Chem. Soc. 99, 1633 (1911), 101, 81, 104 (1912)
7. Stallard, R. D., Amis, E. S., J. A. C. S., 74, 1781 (1952)
8. Dana, L. I., Proc. Amer. Acad., 60, 241 (1925)
9. Tallmadge, J. A., Canjar, L. N., Ind. Eng. Chem., 46, 1279 (1954)
10. Stein, F. P., Martin, J. J., Chem. Eng. Process Symp. Series, V.59, No.44 (1963)
11. Fletcher, J., Tyrer, D., J. Chem. Soc., 103, 516 (1913)
12. Neilson, E. F., White, D., J. Phys. Chem., 63, 1363 (1959)
13. Sage, B. H., Hough, E. W., Anal. Chem., 22, 1304 (1950)
14. Am. Petroleum Inst., Research Project 44, Petroleum Research Laboratory, Carnegie Institute of Technology, "Selected Values of Properties of Hydrocarbons and related Compounds".

REFERENCES (ctd.)

15. Reamer, H. H., Sage, B. H., J. Chem. Eng. Data, 9, 24 (1964).

16. Reamer, H. H., Sage, B. H., Lacey, W. N., Ind. Eng. Chem., 38, 986 (1946).

17. Sage, B. H., Lacey, W. N., "Thermodynamic Properties of the Lighter Paraffin Hydrocarbons and Nitrogen", American Petroleum Institute, New York (1950).

18. Olds, R. H., Sage, B. H., Lacey, W. N., Manuscript 282, "Partial Volumetric Behavior in the n-Butane-decane System", Chem. Eng. Lab., California Institute of Technology,

LIST OF FIGURES

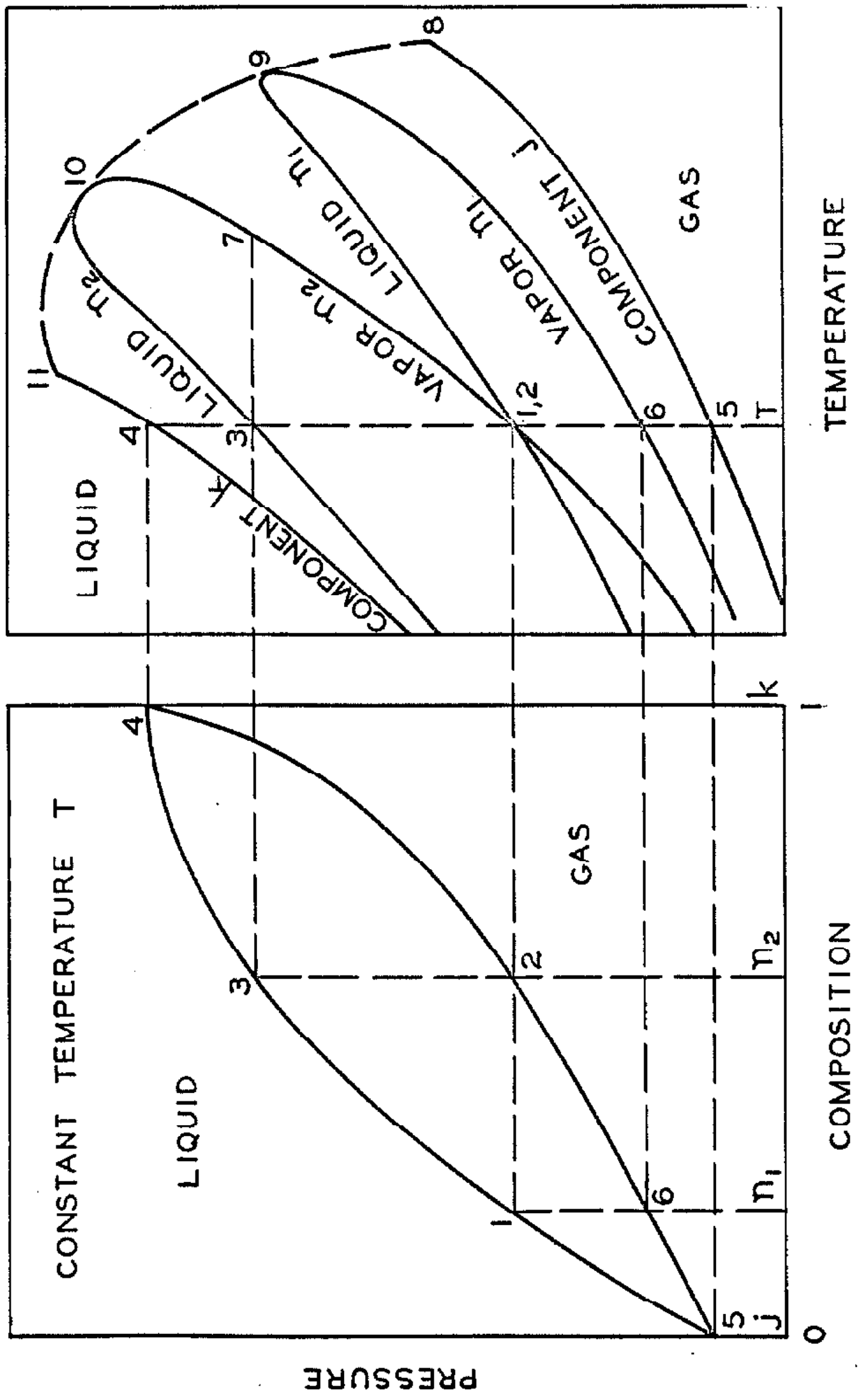

Fig. 1 Pressure-Temperature-Composition Relations for a Binary System

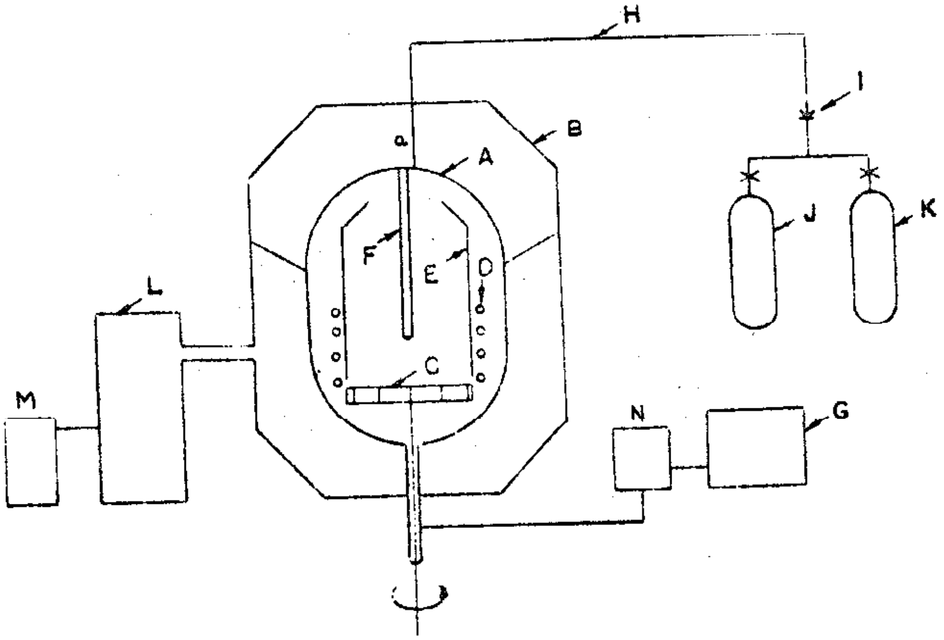

Figure 2. Schematic Arrangement of Equipment

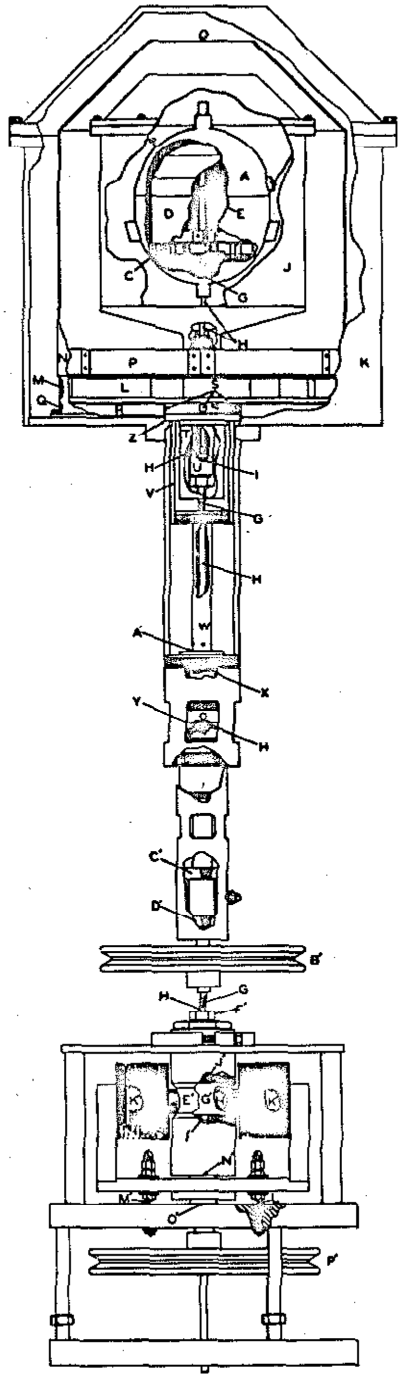

Figure 3 General Arrangement of Equipment

(Courtesy of Analytical Chemistry)

Legend - Figure 3

A	calorimeter bomb
B	agitator
C	ports in circulation shield D
D	circulation shield
E	resistance thermometer
F	radial guide vanes
G	drive shaft for the agitator B
H	tube
I	seal between tube H and sleeve U
J	vacuum jacket
K	oil bath
L	impeller
M	ports in circulation shield N
N	circulation shield
O	opening in circulation shield
P	radial guide vanes
Q	ports in path Q-R-S-T
R	guide vanes
S	ports
T	circulation shield
U	sleeve--part of vacuum jacket

Legend - Figure 3 (cont.)

V, W	sleeve--part of drive for the impeller L
X	packing gland through which the sleeve W leaves the oil bath
Y	packing gland through which the tube H leaves the oil bath
A'	bearing
B'	pulley
C', D'	support bearings for the pulley B'
E'	steel shell
F'	sealing nut between tube H and shell E'
G'	armature housing
I', J'	steel--bronze bearings in which the armature housing rotates
K'	electromagnets
L', M'	slip rings through which the electromagnets are energized
N', O'	support bearings for the electromagnet assembly
P'	pulley to drive the electromagnetic assembly

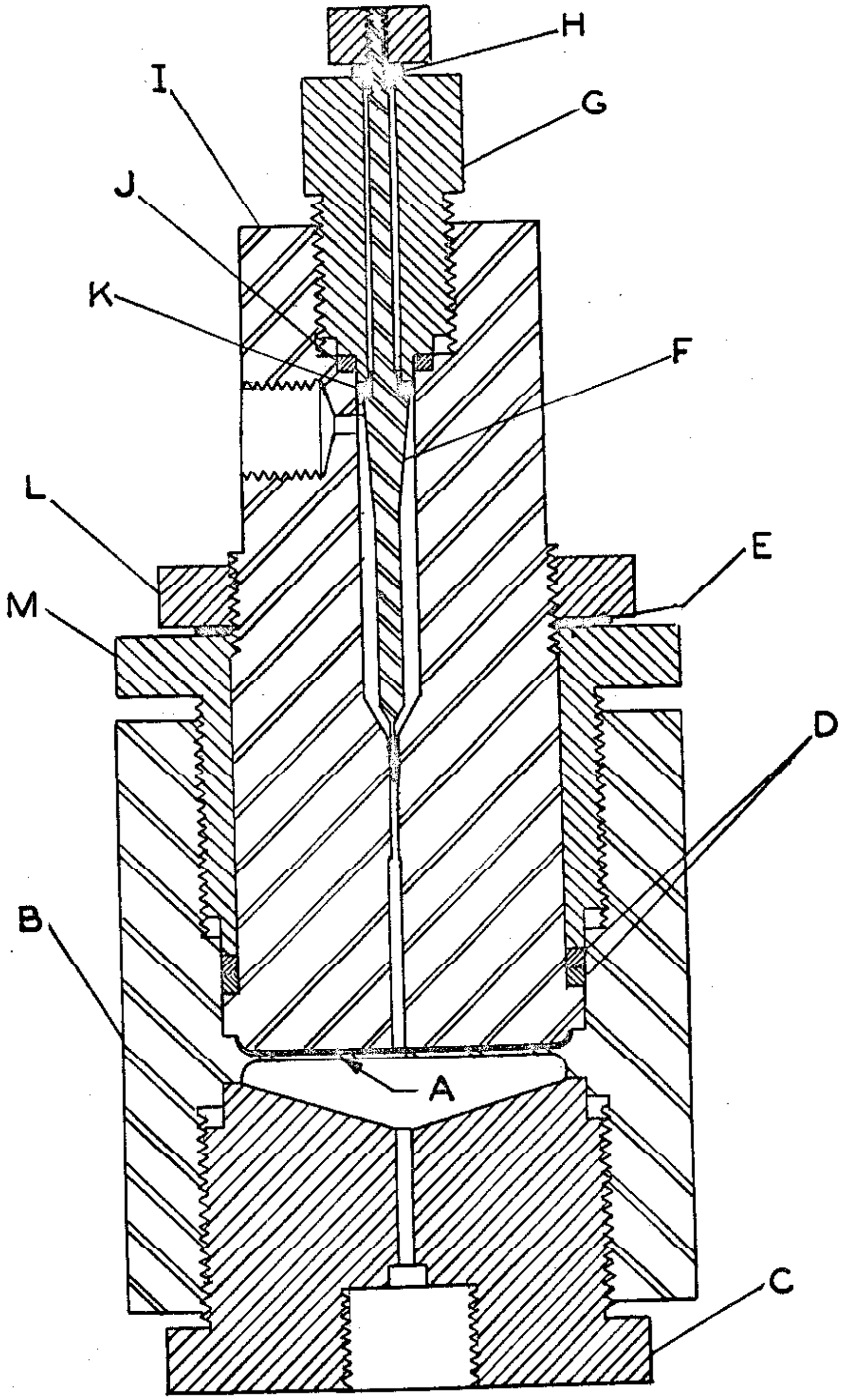

Fig. 4   Diaphragm Block

Legend - Figure 4

A	diaphragm
B	diaphragm cylinder
C	fitting for calorimeter connection
D	copper seal rings
E	metal ring
F	level indicator
G	fitting holding level indicator
H	Bakelite insulator
I	inner cylinder and backing plate for diaphragm
J	copper seal ring
K	Bakelite insulator
L	nut for compressing seal rings D
M	fitting for positioning inner cylinder I

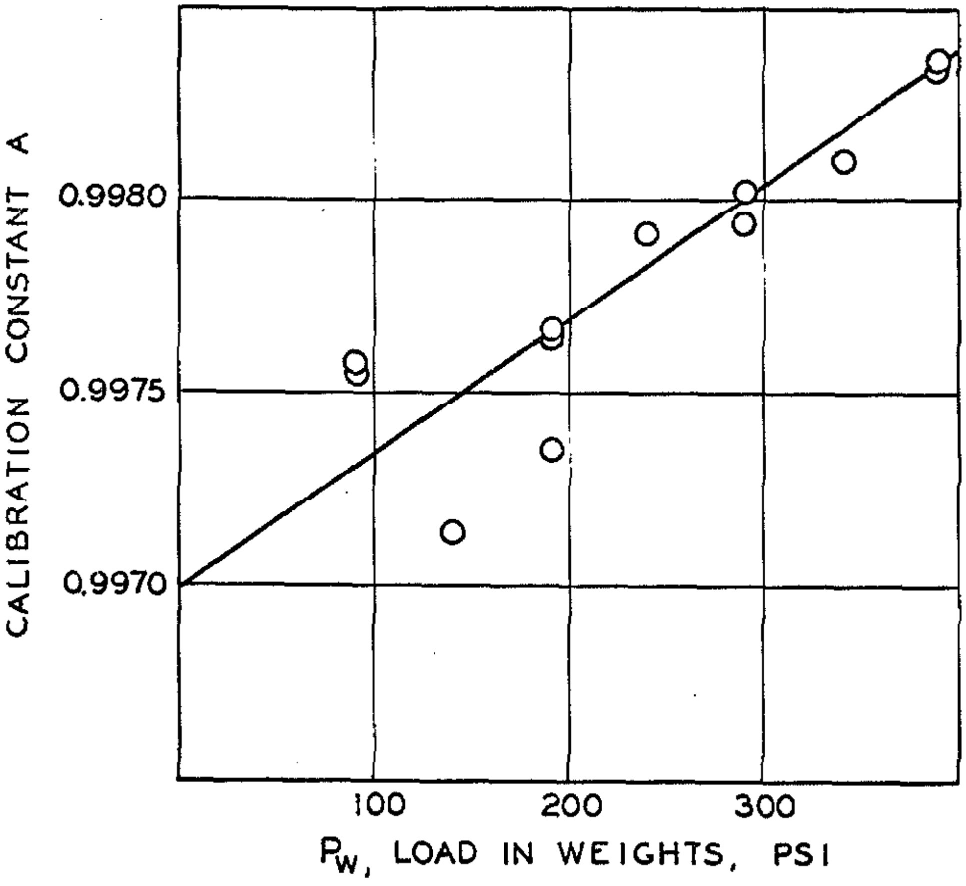

Fig. 5 Calibration Constant A of Ashcroft Gauge Tester

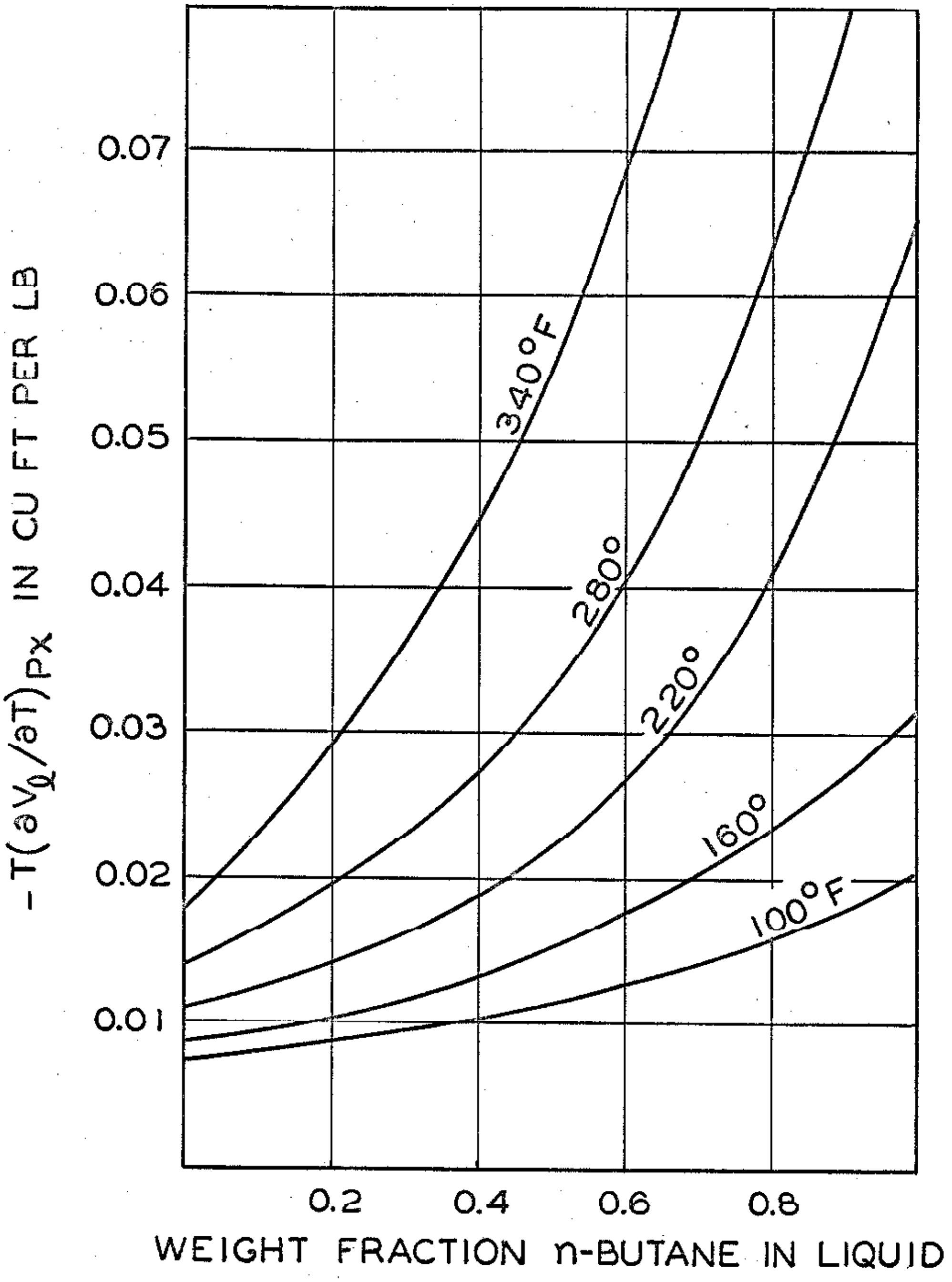

Fig. 6 Latent Heat of Pressure Change for the Bubble-point Liquid

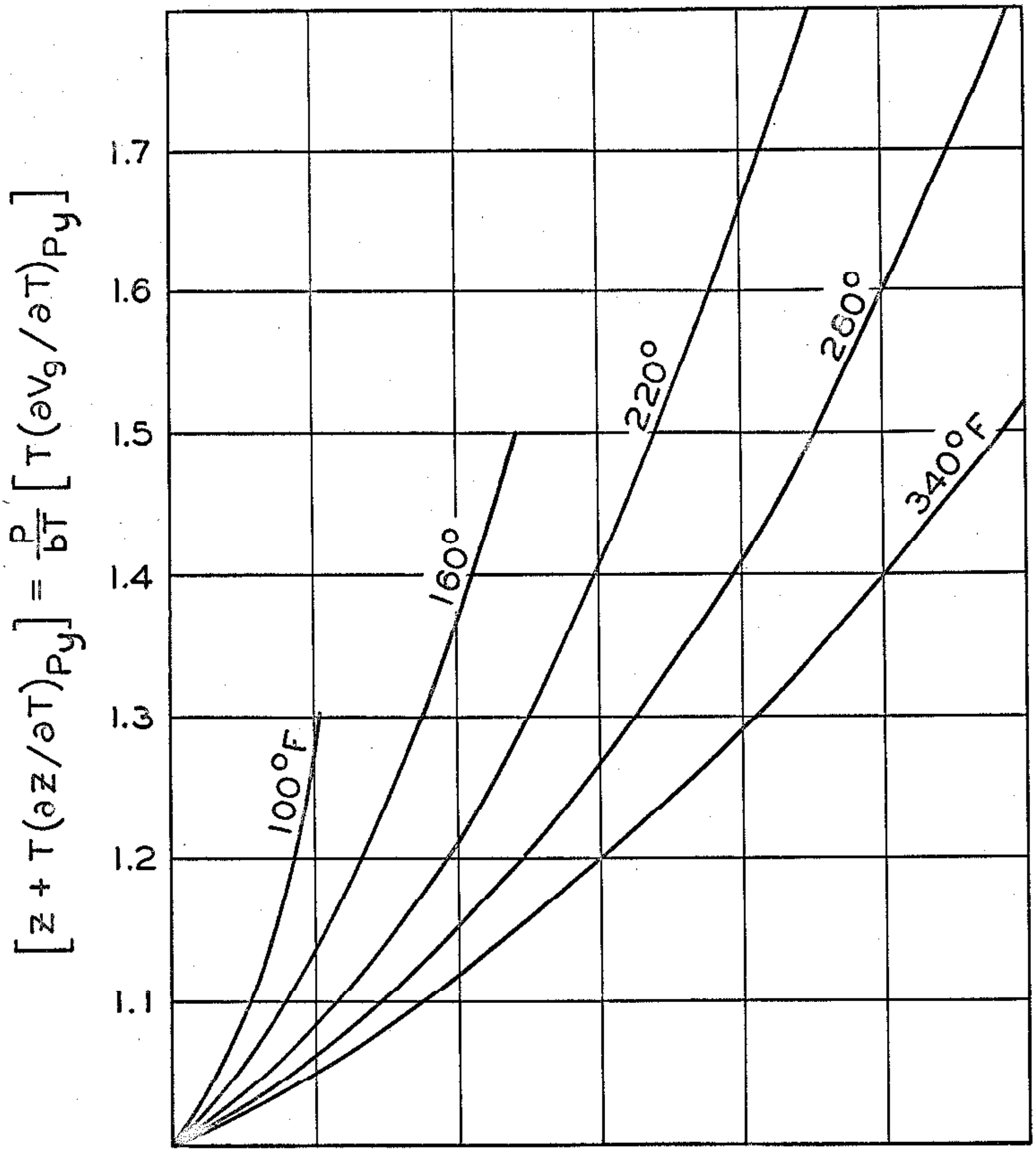

Fig. 7 Factor $-l_P$ P/bT for Dew-point Gas

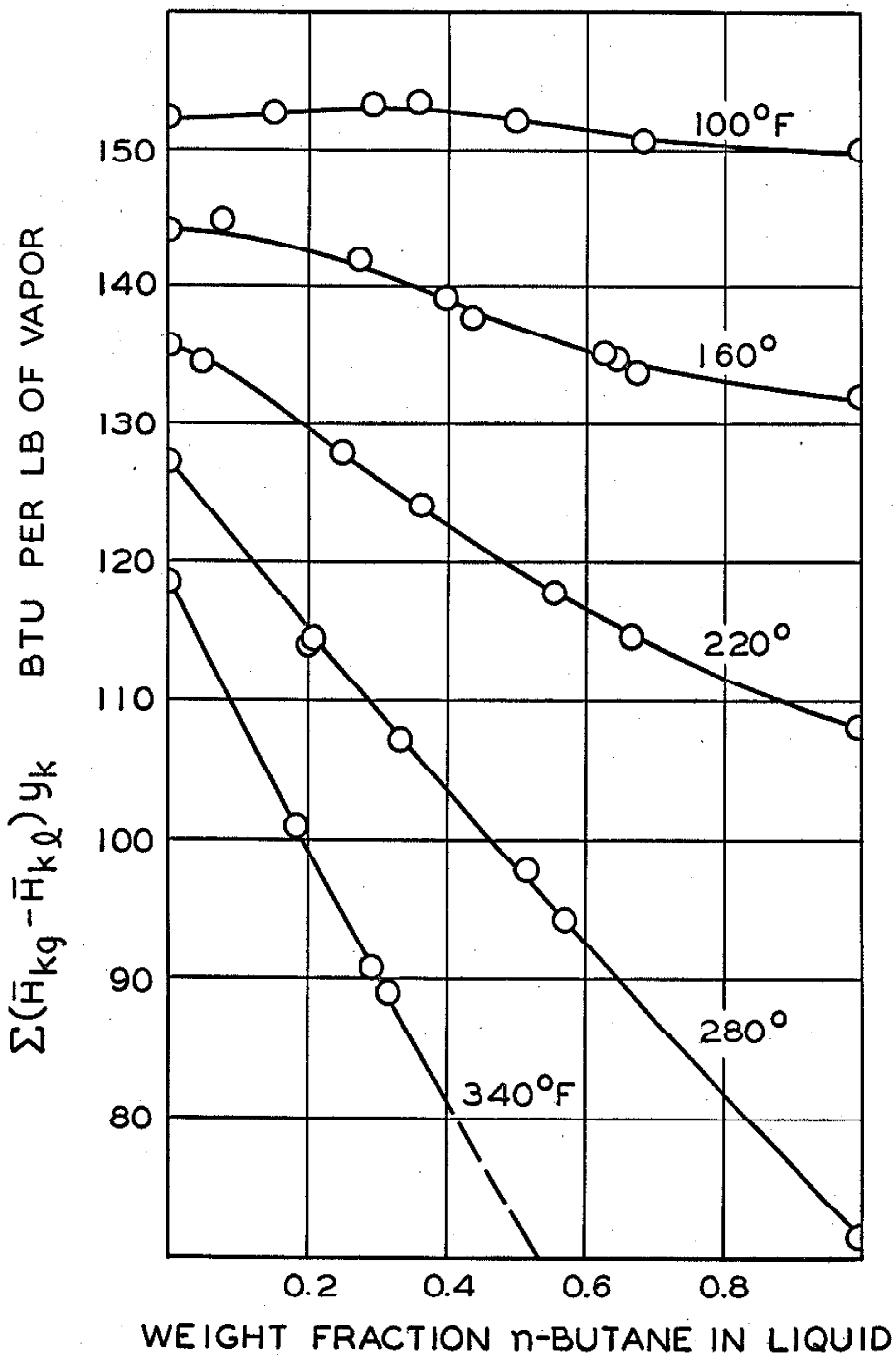

Fig. 8 Enthalpy Change upon Vaporization versus Liquid Composition

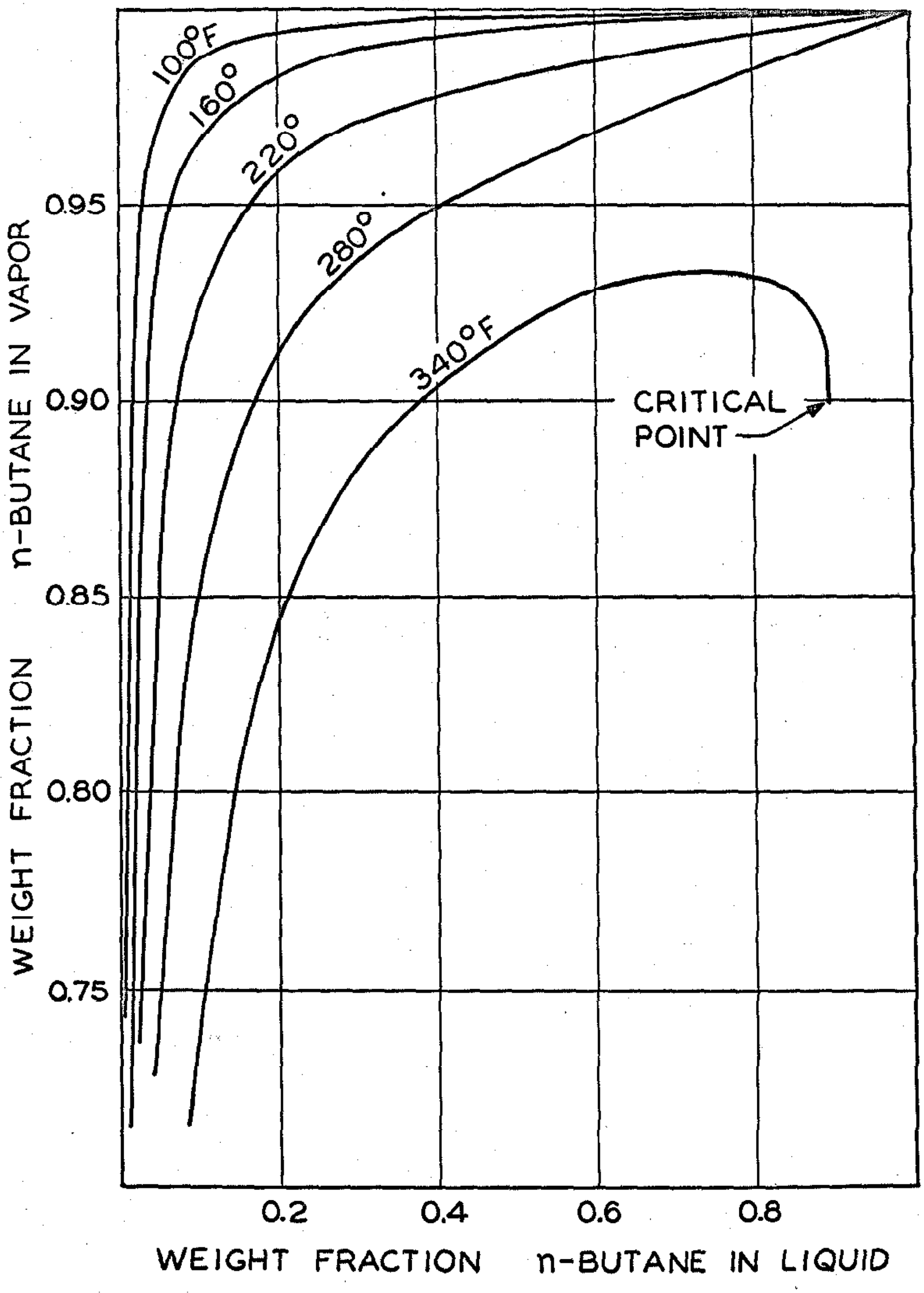

Fig. 9 Vapor-Liquid Composition Diagram

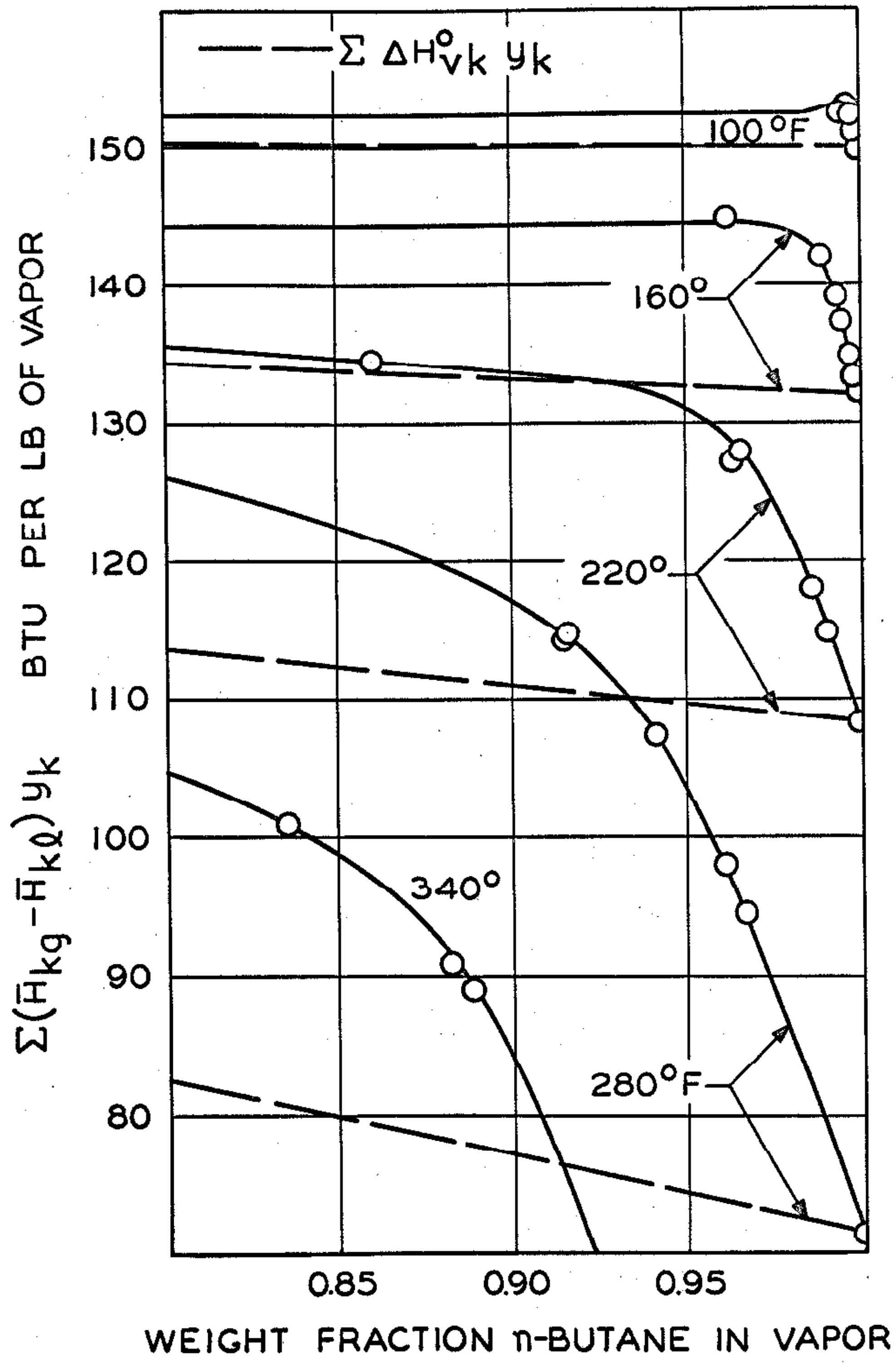

Fig. 10 Enthalpy Change upon Vaporization versus Vapor Composition

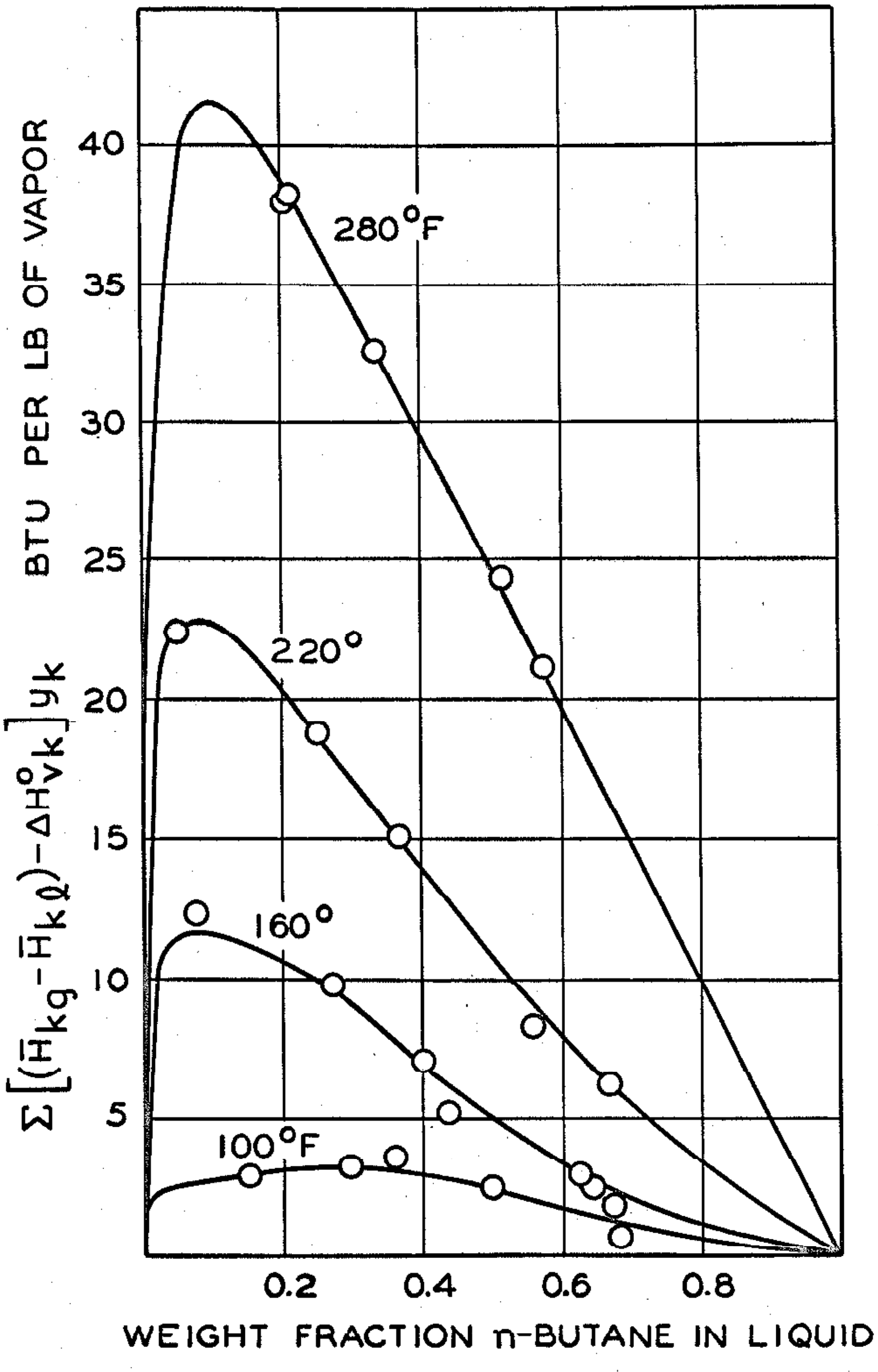

Fig. 11 Residual Enthalpy Change upon Vaporization

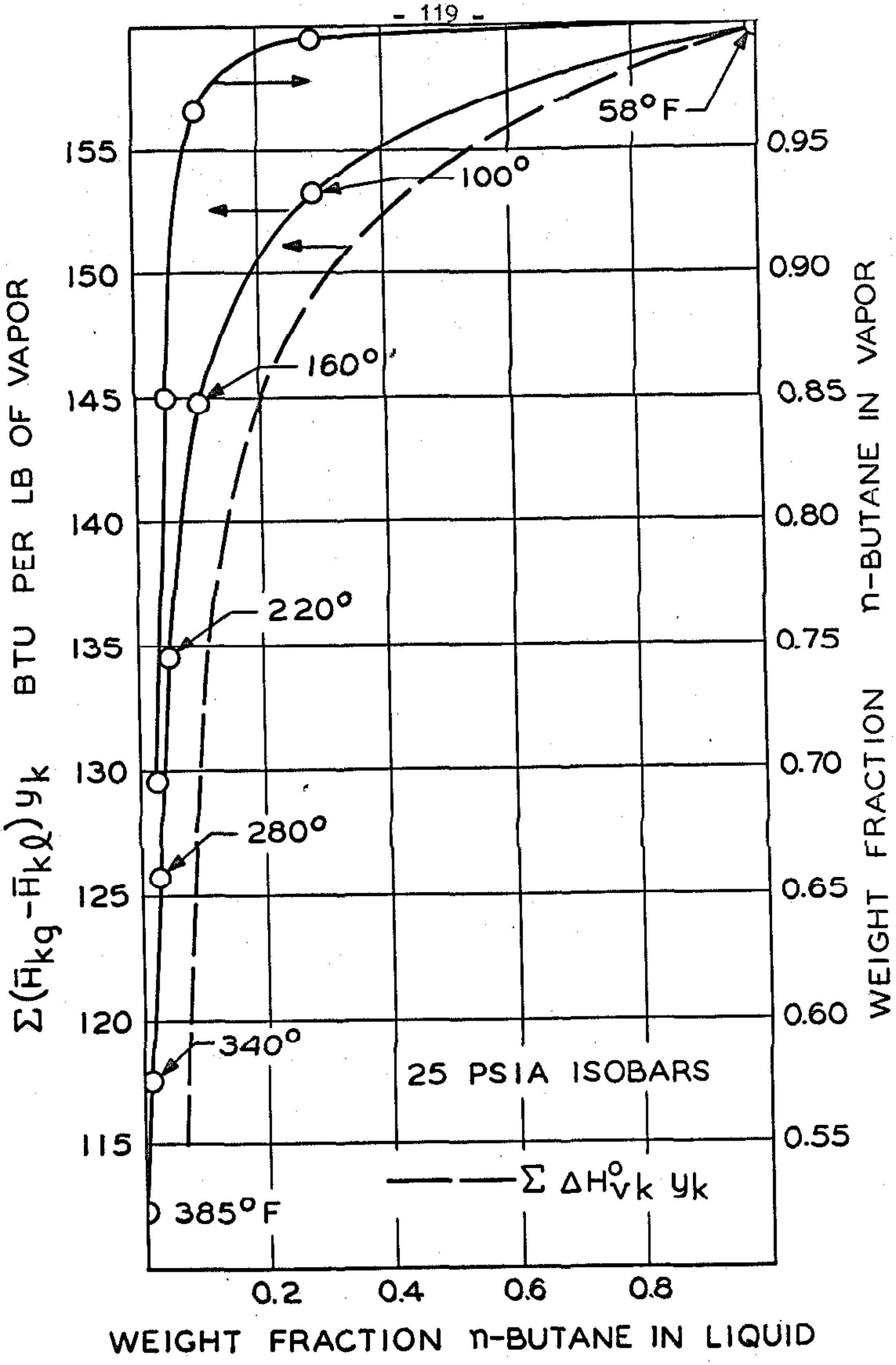

Fig. 12 Enthalpy Change upon Vaporization for the 25 psia Isobar

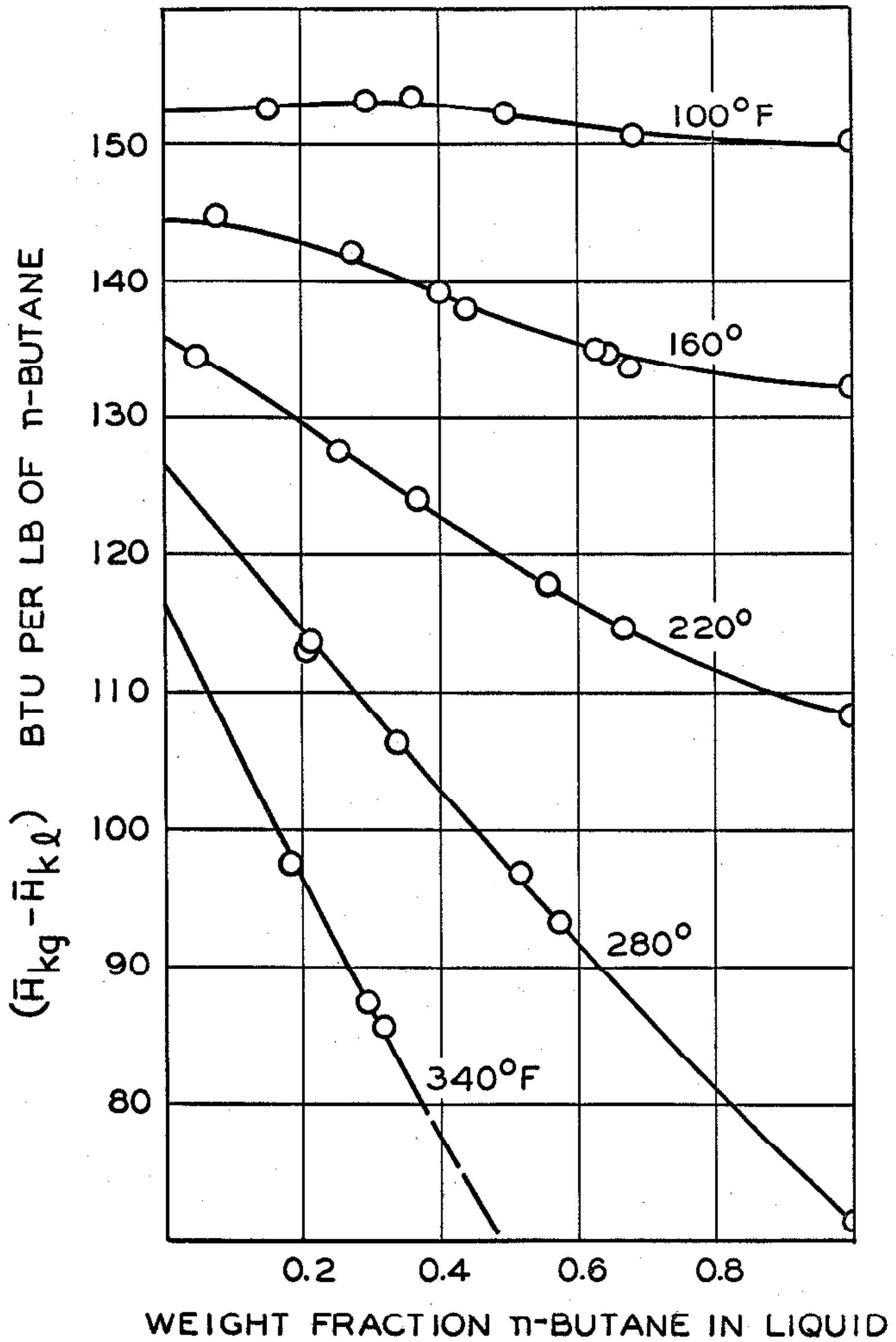

FIG. 13 PARTIAL ENTHALPY CHANGE UPON VAPORIZATION FOR n-BUTANE AS A FUNCTION OF LIQUID COMPOSITION

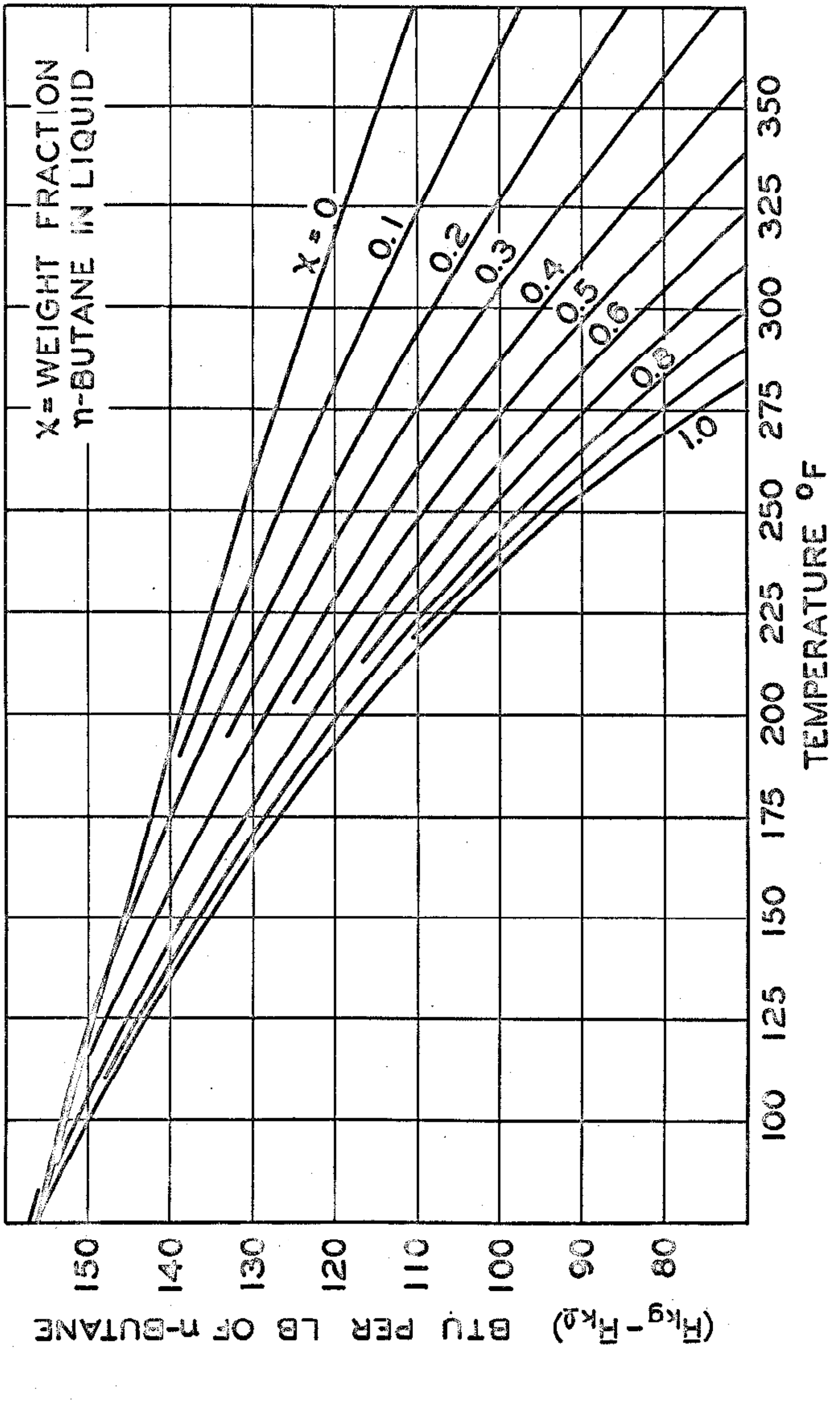

Fig. 14 Partial Enthalpy Change upon Vaporization for n-Butane as a Function of Temperature

LIST OF TABLES

TABLE I EXPERIMENTAL RESULTS

Identification	Pressure, psia		Weight Fraction n-butane	
	P_1	P_2	Vapor	Liquid
100°F				
438	29.4	28.9	0.9985	0.361
447	25.8	25.1	0.9965	0.296
454	15.9	14.5	0.9945	0.150
464	43.0	42.8	0.9995	0.683
473	35.9	35.3	0.9980	0.491
160°F				
448	56.9	54.3	0.9890	0.273
456	23.0	16.5	0.9610	0.075
465	98.4	98.1	0.9980	0.674
476	96.5	95.3	0.9975	0.644
477	94.9	93.9	0.9975	0.626
479	78.1	74.2	0.9945	0.438
480	73.3	70.4	0.9935	0.400
220°F				
442	128.6	126.2	0.9745	0.364
449	100.0	95.4	0.9650	0.249
457	29.1	21.4	0.8595	0.048
467	189.0	187.8	0.9895	0.664
470	169.9	166.6	0.9895	0.554
280°F				
436	140.1	131.5	0.9135	0.205
443	202.5	195.5	0.9410	0.336
451	142.4	134.8	0.9150	0.210
468	296.8	291.7	0.9660	0.570
471	277.3	268.6	0.9600	0.514
340°F				
432	292.0	282.0	0.8875	0.316
433	276.7	264.1	0.8810	0.292
452	196.6	172.6	0.8345	0.183

TABLE I EXPERIMENTAL RESULTS (Ctd.)

Identification	Energy Added Btu			$\underline{l}_p$[a] ΔP
	Electric Q_e	Agitation Q_s	Cond.& Rad. Q_{c+r}	Btu
100°F				
438	3.0634	0.0828	0.0031	0.0028
447	3.2405	0.1121	0.0055	0.0033
454	3.6904	0.0804	-0.0034	0.0075
464	5.1604	0.0714	-0.0034	0.0011
473	3.5366	0.0736	0.0021	0.0007
160°F				
448	5.2611	0.1011	-0.0007	0.0141
456	4.9115	0.1216	0.0034	0.0350
465	2.7269	0.0589	0.0061	0.0020
476	6.9125	0.0517	0.0073	0.0087
477	5.4651	0.0469	-0.0065	0.0075
479	7.1264	0.0627	-0.0083	0.0324
480	4.4975	0.0418	-0.0021	0.0249
220°F				
442	5.3938	0.0371	0.0004	0.0197
449	3.9790	0.0420	-0.0037	0.0288
457	2.8639	0.1074	-o.0003	0.0563
467	3.5429	0.0341	0.0030	0.0111
470	4.7875	0.0453	-0.0005	0.0325
280°F				
436	2.6568	0.0411	0.0014	0.0728
443	3.2927	0.0314	-0.0021	0.0633
451	3.1199	0.0524	-0.0024	0.0561
468	3.5315	0.0157	-0.0004	0.0616
471	4.6182	0.0258	0.0030	0.1125
340°F				
432	2.7101	0.0459	0.0094	0.1179
433	3.1692	0.0576	-0.0013	0.1501
452	5.3103	0.1095	-0.0051	0.2053

[a] $\underline{l}_P = -\left\{ m_g T\,(\partial V_g/\partial T)_{P,y} + m_l\, T(\partial V_l/\partial T)_{P,x} \right\}$

TABLE I EXPERIMENTAL RESULTS (Ctd.)

Identification	Material Withdrawn	Vaporized, lb		Calorimeter Contents
		Change in Vapor weight		
	Δ m	$\Delta m_{k,g}$[b]	$\Delta m_{j,g}$[b]	m_2, lb
100°F				
438	0.020386	0.00011	0.00000	1.2338
447	0.021821	0.00008	0.00000	1.4777
454	0.024803	-0.00014	-0.00001	1.1984
464	0.034274	0.00044	0.00000	1.4603
473	0.023607	0.00009	0.00001	0.8992
160°F				
448	0.037332	0.00033	0.00000	1.4251
456	0.035531	-0.00100	-0.00001	1.0934
465	0.020314	0.00057	0.00000	1.4280
476	0.050321	0.00142	0.00000	1.2736
477	0.039692	0.00104	0.00000	1.2171
479	0.051903	0.00013	0.00002	0.8060
480	0.032489	-0.00011	0.00002	0.7629
220°F				
442	0.042451	0.00049	0.00002	1.2469
449	0.030620	0.00050	0.00004	1.3846
457	0.022871	-0.00125	0.00003	1.0669
467	0.029020	0.00205	0.00003	1.3836
470	0.038910	0.00170	0.00006	1.0426
280°F				
436	0.023632	-0.00071	0.00006	1.0063
443	0.029289	0.00095	0.00009	1.1933
451	0.026808	0.00030	0.00009	1.3144
468	0.033421	0.00334	0.00015	1.0978
471	0.043432	0.00262	0.00019	0.9687
340°F				
432	0.027816	0.00159	0.00032	1.1858
433	0.032292	0.00120	0.00031	1.1392
452	0.050655	0.00040	0.00045	1.2489

---

[b] Component j = n-Decane, Component k = n-Butane

TABLE I EXPERIMENTAL RESULTS (Ctd.)

Identification	Estimated[b] $(\bar{H}_{j,g}-\bar{H}_{j,l})$ Btu/lb	$(\bar{H}_{j,g}-\bar{H}_{j,l})\,y_j$ Btu/lb	$\sum_{k=1}^{2}(\bar{H}_{k,g}-\bar{H}_{k,l})\,y_k$ Btu/lb	n-Butane $(\bar{H}_{k,g}-\bar{H}_{k,l})$ Btu/lb
100°F				
438	151.9	0.2	153.5	153.5
447	152.0	0.5	153.2	153.2
454	152.2	0.8	152.5	152.5
464	151.7	0.1	150.6	150.6
473	151.8	0.3	152.3	152.3
160°F				
448	143.4	0.2	142.0	142.0
456	144.0	0.6	144.9	144.7
465	142.7	0.3	133.8	133.6
476	142.7	0.4	134.6	134.6
477	142.8	0.4	135.0	135.0
479	143.1	0.8	137.3	137.3
480	143.1	0.9	139.3	139.2
220°F				
442	133.9	3.4	124.2	124.0
449	134.4	4.7	128.0	127.8
457	135.5	19.0	134.6	134.5
467	133.1	1.4	114.8	114.6
470	133.4	1.4	118.0	117.8
280°F				
436	125.7	10.9	114.2	113.1
443	124.7	7.4	107.4	106.3
451	125.6	10.7	114.5	113.4
468	123.4	4.2	94.4	93.2
471	123.7	5.0	98.0	97.0
340°F				
432	115.4	13.0	89.0	85.6
433	115.7	13.8	90.9	87.5
452	116.8	19.3	101.0	97.5

[b] Component j = n-Decane, Component k = n-Butane

TABLE II PARTIAL ENTHALPY CHANGE UPON VAPORIZATION FOR n-BUTANE, BTU/LB.

Wt. Fraction n-Butane in Liquid	Temperature °F					
	70	100	130	160	190	220
0.0	156.4	152.4	148.3	144.2	140.1	135.8
0.1	156.6	152.6	148.4	143.9	138.6	132.9
0.2	157.1	153.0	148.4	143.0	136.0	129.5
0.3	157.6	153.2	147.7	141.2	134.0	126.1
0.4	157.7	153.0	146.5	139.0	131.2	122.8
0.5	157.3	152.2	144.9	136.9	128.6	119.5
0.6	156.6	151.5	143.9	135.2	126.1	116.4
0.7	156.4	150.7	142.9	134.0	124.4	113.7
0.8	156.5	150.3	142.4	133.2	123.2	111.5
0.9	156.9	150.1	141.9	132.7	122.2	109.7
1.0	157.2	149.9	141.4	132.1	121.1	108.3

TABLE II PARTIAL ENTHALPY CHANGE UPON VAPORIZATION FOR n-BUTANE, BTU/LB. (Ctd.)

Wt. Fraction n-Butane in Liquid	Temperature °F				
	250	280	310	340	370
0.0	131.2	126.4	121.4	116.3	111.1
0.1	126.7	120.1	113.2	105.9	98.5
0.2	122.0	114.0	105.2	96.0	86.2
0.3	117.7	108.3	97.9	86.8	74.8
0.4	113.3	102.7	90.7	78.0	64.3
0.5	109.1	97.2	83.8	69.1	-
0.6	105.0	91.9	77.2	-	-
0.7	101.2	86.6	70.4	-	-
0.8	97.6	81.4	-	-	-
0.9	94.6	76.4	-	-	-
1.0	92.3	71.5	-	-	-

TABLE III PARTIAL INTERNAL ENERGY CHANGE UPON VAPORIZATION FOR n-BUTANE, BTU/LB

Wt. Fraction n-Butane in Liquid	Temperature °F					
	70	100	130	160	190	220
0.0	138.2	133.3	128.1	123.0	117.9	112.6
0.1	138.7	133.9	128.8	123.6	117.8	111.4
0.2	139.4	134.6	129.3	123.3	116.7	109.6
0.3	140.1	135.1	129.0	122.0	114.8	107.1
0.4	140.4	135.1	128.1	120.3	112.6	104.4
0.5	140.1	134.6	126.8	118.6	110.5	101.9
0.6	139.5	133.9	126.0	117.2	108.8	99.4
0.7	139.4	133.3	125.2	116.4	107.5	97.3
0.8	139.6	133.0	124.9	115.9	106.4	95.7
0.9	140.0	132.7	124.6	115.6	105.5	94.3
1.0	140.4	132.8	124.3	115.3	104.9	93.3

TABLE III PARTIAL INTERNAL ENERGY CHANGE UPON VAPORIZATION FOR n-BUTANE, BTU/LB (Ctd.)

Wt. Fraction n-Butane in Liquid	Temperature °F				
	250	280	310	340	370
0.0	107.0	101.3	95.7	90.2	84.7
0.1	104.5	97.2	90.0	81.9	73.3
0.2	101.6	93.2	84.5	74.7	64.2
0.3	98.5	89.2	79.0	68.2	56.1
0.4	95.2	85.1	73.9	61.9	48.8
0.5	92.0	81.0	68.8	55.4	-
0.6	88.9	76.9	63.6	-	-
0.7	85.9	72.9	58.8	-	-
0.8	83.2	68.9	-	-	-
0.9	81.0	65.1	-	-	-
1.0	79.1	61.5	-	-	-

TABLE IV ESTIMATED UNCERTAINTIES OF MEASUREMENT

Quantity	Probable Uncertainty per cent
Energy added electrically	0.03
Energy added by agitation	0.12
Energy exchange between calorimeter and jacket	0.01
Energy effect of pressure drop	0.04
Change in temperature of liquid and vapor	0.03
Weight of material withdrawn	0.02
Change in weight of vapor phase	0.10
Effects due to deviation from equilibrium	0.05

APPENDIX

Comments on Calorimeter Analysis of Previous Investigators

McKay (1) has published the following general expression for vaporization of a one-component system from an isochoric vessel :

$$
\begin{aligned}
(H_d - H_b)^* = {} & \frac{1}{\displaystyle\int_{m_1}^{m_2} \frac{V_g + m_g \frac{dV_g}{dm} + m_\ell \frac{dV_\ell}{dm}}{V_g - V_\ell}\, dm} \\
& \Bigg[\int_1^2 -q + \int_{m_1}^{m_2} \Big\{ m_\ell \Big[\ell_p - P \Big(\frac{\partial V}{\partial P}\Big)_T \Big]_\ell + \\
& m_g \Big[\ell_p - P \Big(\frac{\partial V}{\partial P}\Big)_T \Big]_g \Big\} \frac{dP}{dm}\, dm + \\
& \int_{m_1}^{m_2} \Big\{ m_\ell \Big[C_p - P \Big(\frac{\partial V}{\partial T}\Big)_P \Big]_\ell + m_g \Big[C_p - P \Big(\frac{\partial V}{\partial T}\Big)_P \Big]_g + \\
& - C_c \Big\} \frac{dT}{dm}\, dm + \\
& + \int_{m_1}^{m_2} P \Big(m_g \frac{dV_g}{dm} + m_\ell \frac{dV_\ell}{dm} \Big)\, dm + \\
& \int_{m_1}^{m_2} \frac{\{(H_g - H_d) - (H_\ell - H_b)\} \Big(V_g + m_g \frac{dV_g}{dm} + m_\ell \frac{dV_\ell}{dm}\Big)}{V_g - V_\ell}\, dm \Bigg]
\end{aligned}
\tag{1}
$$

Equation (1) can be presented in a simpler form since several terms actually cancel each other. The next to last term may be written as :

$$\int_{m_1}^{m_2} P \left(m_g \frac{dV_g}{dm} + m_l \frac{dV_l}{dm} \right) dm =$$

$$\int_{m_1}^{m_2} \left\{ m_l P \left(\frac{\partial V_l}{\partial P}\right)_T + m_g P \left(\frac{\partial V_g}{\partial P}\right)_T \right\} \frac{dP}{dm} \, dm$$

$$+ \int_{m_1}^{m_2} \left\{ m_l P \left(\frac{\partial V_l}{\partial T}\right)_P + m_g P \left(\frac{\partial V_g}{\partial T}\right)_P \right\} \frac{dT}{dm} \, dm \qquad (2)$$

Substitution of Equation (2) into Equation (1) and rearranging results in

$$(H_a - H_b)^* = \frac{1}{\displaystyle\int_1^2 \frac{V_g \, dm + m_g \, dV_g + m_l \, dV_l}{V_g - V_l}}$$

$$\left[\int_1^2 -\underline{q} + \int_1^2 (m_l \, l_{P,l} + m_g \, l_{P,g}) \, dP \right.$$

$$\left. + \int_1^2 (m_l \, c_{P,l} + m_g \, c_{P,g} + c_c) \, dT \right]$$

$$- \left\{ (H_g - H_a) - (H_l - H_b) \right\}^* \qquad (3)$$

In Equation (1) the sign of C_c and the sign of the last term are in error; they have been corrected in Equation (3). By applying Equation (34) of Part III to a one-component system Equation (3) can be obtained directly.

For the case of a binary system with only one volatile component McKay gives the following equation in Manuscript 5143.1 (2) :

$$(H^{\circ}_{k,d} - \bar{H}_{k,b})^{*} = \frac{1}{\displaystyle\int_{m_1}^{m_2} \frac{V^{\circ}_{k,g} + m_{k,g}\dfrac{dV^{\circ}_{k,g}}{dm} + m_{k,\ell}\dfrac{d\bar{V}_{k,\ell}}{dm} + m_{j,\ell}\dfrac{d\bar{V}_{j,\ell}}{dm}}{V^{\circ}_{k,g} - \bar{V}_{k,\ell}}\, dm}$$

$$\Bigg[\int_{1}^{2} -\underline{q} + \int_{m_1}^{m_2} \left\{ m_\ell \left[\ell_p - P\left(\frac{\partial V}{\partial P}\right)_{T,n} \right]_\ell + m_g \left[\ell_p - P\left(\frac{\partial V}{\partial P}\right)_{T,n} \right]_g \right\} \frac{dP}{dm}\, dm$$

$$+ \int_{m_1}^{m_2} \left\{ m_\ell \left[C_p - P\left(\frac{\partial V}{\partial T}\right)_{P,n} \right]_\ell + m_g \left[C_p - P\left(\frac{\partial V}{\partial T}\right)_{P,n} \right]_g - C_c \right\} \frac{dT}{dm}\, dm$$

$$+ \int_{m_1}^{m_2} P \left(m_{k,g}\frac{dV^{\circ}_{k,g}}{dm} + m_{k,\ell}\frac{d\bar{V}_{k,\ell}}{dm} + \frac{m_{j,\ell}\, d\bar{V}_{j,\ell}}{dm} \right) dm$$

$$+ \int_{m_1}^{m_2} \frac{\left[(H^{\circ}_{k,g} - H^{\circ}_{k,d}) - (\bar{H}_{k,\ell} - \bar{H}_{k,b}) \right] \left(V^{\circ}_{k,g} + m_{k,g}\dfrac{dV^{\circ}_{k,g}}{dm} + m_{k,\ell}\dfrac{d\bar{V}_{k,\ell}}{dm} + m_{j,\ell}\dfrac{d\bar{V}_{j,\ell}}{dm} \right)}{V^{\circ}_{k,g} - \bar{V}_{k,\ell}}\, dm \Bigg] \qquad (4)$$

By considering the fact that the total calorimeter volume is constant it can be shown that several terms in Equation (4) again cancel each other :

$$\underline{V} = m_{k,g} V^{\circ}_{k,g} + m_{k,\ell} \bar{V}_{k,\ell} + m_{j,\ell} \bar{V}_{j,\ell} = \text{constant} \quad (5)$$

Differentiation yields

$$m_{k,g}\, dV^{\circ}_{k,g} + m_{k,\ell}\, d\bar{V}_{k,\ell} + m_{j,\ell}\, d\bar{V}_{j,\ell} = - V^{\circ}_{k,g}\, dm_{k,g} - \bar{V}_{k,\ell}\, dm_{k,\ell} \quad (6)$$

The total volume may be expressed in another way :

$$\underline{V} = \underline{V}_g + \underline{V}_\ell = \text{constant} \quad (7)$$

Differentiation yields

$$\left\{ m_g \left(\frac{\partial V_g}{\partial T}\right)_{P,n} + m_\ell \left(\frac{\partial V_\ell}{\partial T}\right)_{P,n} \right\} dT + \left\{ m_g \left(\frac{\partial V_g}{\partial P}\right)_{T,n} + m_\ell \left(\frac{\partial V_\ell}{\partial T}\right)_{T,m} \right\} dP = - \bar{V}_{k,g}\, dm_{k,g} - \bar{V}_{k,\ell}\, dm_{k,\ell} \quad (8)$$

Combine Equations (6) and (8) :

$$\left(m_{k,g}\, dV^{o}_{k,g} + m_{k,l}\, d\bar{V}_{k,l} + m_{j,l}\, d\bar{V}_{j,l} \right) =$$

$$\left\{ m_g \left(\frac{\partial V_g}{\partial T}\right)_{P,m} + m_l \left(\frac{\partial V_l}{\partial T}\right)_{P,m} \right\} dT \; +$$

$$\left\{ m_g \left(\frac{\partial V_g}{\partial P}\right)_{T,m} + m_l \left(\frac{\partial V_l}{\partial P}\right)_{T,m} \right\} dP \qquad (9)$$

Replacing the next to last term of Equation (4) by Equation (9) results in the cancellation of several terms and Equation (4) becomes

$$\left(H^{o}_{k,d} - \bar{H}_{k,l}\right)^{*} = \frac{1}{\displaystyle\int_1^2 \frac{V^{o}_{k,g}\, dm + m_{k,g}\, dV^{o}_{k,g} + m_{k,l}\, d\bar{V}_{k,l} + m_{j,l}\, d\bar{V}_{j,l}}{V^{o}_{k,g} - \bar{V}_{k,l}}}$$

$$\left[\int_1^2 \underline{q} + \int_1^2 \left\{ m_l\, l_{P,l} + m_g\, l_{P,g} \right\} dP \right.$$

$$\left. + \int_1^2 \left(m_l\, c_{P,l} + m_g\, c_{P,g} + c_c \right) dT \right]$$

$$- \left\{ \left(H^{o}_{k,g} - H^{o}_{k,d} \right) - \left(\bar{H}_{k,l} - \bar{H}_{k,b} \right) \right\}^{*}$$

(10)

As before the sign of C_c and the sign of the last term of Equation (4) have been corrected. Equation (10) contains the partial volumes for both components in the liquid phase. The use of partial volumes can be avoided and Equation (10) can be further simplified by using the following equality :

$$\left(\frac{\overset{\circ}{V}_{k,g} + m_{k,g} \frac{d\overset{\circ}{V}_{k,g}}{dm} + m_{k,l} \frac{d\bar{V}_{k,l}}{dm} + m_{j,l} \frac{d\bar{V}_{j,l}}{dm}}{\overset{\circ}{V}_{k,g} - \bar{V}_{k,l}} \right) dm =$$

$$dm - dm_{k,g} = dm_{k,l} =$$

$$\left(\frac{\overset{\circ}{V}_{k,g} + m_{k,g} \frac{d\overset{\circ}{V}_{k,g}}{dm} + m_{l} \frac{dV_{l}}{dm}}{\overset{\circ}{V}_{k,g} - V_{l}} \right) dm \qquad (11)$$

Substitution of Equation (11) into Equation (10) and rearranging results in :

$$\left(H^{\circ}_{k,d} - \bar{H}_{k,b}\right)^{*} = \frac{1}{\int_{1}^{2} \frac{V_g \, dm + m_g \, dV_g + m_\ell \, dV_\ell}{V_g - V_\ell}}$$

$$\left[\int_{1}^{2} - \underline{q} + \int_{1}^{2} \left(m_\ell \, l_{P,\ell} + m_g \, l_{P,g}\right) dP \right.$$

$$\left. + \int_{1}^{2} \left(m_\ell \, C_{P,\ell} + m_g \, C_{P,g} + C_c\right) dT \right]$$

$$- \left\{ \left(H^{\circ}_{k,g} - H^{\circ}_{k,d}\right) - \left(\bar{H}_{k,\ell} - H_{k,b}\right) \right\}^{*} \tag{12}$$

The same result was obtained in a more direct manner as Equation (44) of Part III.

References

(1) "Latent Heat of Vaporization for n-Octane", R. A. McKay and B. H. Sage, Journal of Chemical and Engineering Data, Vol. 5, No. 1, p. 22 (Jan. 1960)

(2) Manuscript 5143.1 Supplementary material for article on "Latent Heat of Vaporization for n-Octane", R. A. McKay and B. H. Sage, April 1959, Chemical Engineering Laboratory, California Institute of Technology.

PROPOSITIONS

PROPOSITION I

It is proposed that a generalized chart be constructed showing $l_p\ (-P_c/T_c)$ as a function of reduced pressure and reduced temperature. This "generalized l_p chart" can be easily constructed from the generalized compressibility factor chart according to the formula

$$\ell_p\left(-P_c/T_c\right) = \frac{R\,T_r}{P_r}\left\{ z + T_r\left(\frac{\partial z}{\partial T_r}\right)_{P_r} \right\}$$

Introduction

For systems of constant composition and weight the heat transfer q across the boundary of the system can be computed from

$$(q + \dot{j}) = C_p\, dT + \ell_p\, dP \tag{1}$$

Values of C_p can be found in the literature for many substances at numerous states. Listings of l_p are seldom available.

The latent heat of pressure change is defined as

$$\ell_p = \left(\frac{q + \dot{j}}{dP}\right)_T \tag{2}$$

and C_p is defined as

$$C_p = \left(\frac{q + \dot{j}}{dT}\right)_P \tag{3}$$

Thus l_P is similar in nature to C_P except that it applies to the case in which the temperature is held constant while the pressure changes rather than the reverse. It can be shown (1) that

$$\ell_P = - T \left(\partial V / \partial T \right)_P \qquad (4)$$

l_P can thus be evaluated from a knowledge of the PVT relations of the system in question. A generalized PVT relation is available in the form of the generalized compressibility factor chart. This chart gives the compressibility factor z as a function of reduced pressure and reduced temperature. It is based on two assumptions :

1. The law of corresponding states applies, i.e. all gases have the same reduced volume at equivalent reduced temperatures and pressures.
2. All gases have the same critical compressibility factor $z_c = P_c V_c / R T_c$. For systems that follow these requirements, l_P can be calculated from the generalized compressibility factor chart and the critical (or pseudo-critical) properties of the system. These calculations can be done once and for all by preparing a "generalized l_P chart".

Derivation

The PVT relationship

$$P V = z R T \qquad (5)$$

may be differentiated to give

$$P\, dV + V\, dP = z R\, dT + R T\, dz \qquad (6)$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{zR}{P} + \frac{RT}{P}\left(\frac{\partial z}{\partial T}\right)_P = \frac{R}{P}\left\{ z + T\left(\frac{\partial z}{\partial T}\right)_P \right\} \tag{7}$$

This can be written in generalized form by substituting

$$T = T_c \; T_r \tag{8}$$

to yield

$$\left(\partial V/\partial T\right)_P = \frac{R}{P}\left\{ z + T_r \left(\partial z/\partial T_r\right)_{P_r} \right\} \tag{9}$$

Substitute Equation (9) into Equation (4) :

$$\left(- \frac{P}{T}\right) \ell_P = R\left\{ z + T_r \left(\frac{\partial z}{\partial T_r}\right)_{P_r} \right\} \tag{10}$$

The right-hand side of Equation (10) consists of generalized properties and can be evaluated as a function of P_r and T_r. Equation (10) can be presented in a slightly different form by substituting

$$P = P_c \; P_r \tag{11}$$

and Equation (8) into Equation (10) :

$$\ell_P\left(- P_c / T_c\right) = \frac{R\,T_r}{P_r}\left\{ z + T_r \left(\frac{\partial z}{\partial T_r}\right)_{P_r} \right\} \tag{12}$$

l_p $(-P_c/ T_c)$ can be plotted versus T_r as lines of constant P_r or versus P_r as lines of constant T_r, whichever method is best.

Once this chart has been constructed, the l_p of any system whose PVT behavior is given by the generalized compressibility factor chart can be quickly obtained by computing P_r and T_r and reading the value of l_p $(-P_c/T_c)$ from the chart.

References

1. Lacey, W. N., Sage, B. H., "Thermodynamics of One-component Systems", Acadamic Press Inc., New York (1957), p.57.

Nomenclature

Symbols

C_P	molal heat capacity at constant pressure, Btu/lb mole
j	specific differential quantity of friction, Btu/lb mole
l_P	latent heat of pressure change, Btu/lb mole
P	pressure, lb/in.^{2}, psia
q	specific differential quantity of heat transferred to the system, Btu/lb mole
R	gas constant, Btu/lb mole, $^\circ$R
T	absolute temperature, $^\circ$R
V	specific volume, ft.^{3}/lb mole
z	compressibility factor; PV/RT

Subscripts

c	critical value
r	reduced value

PROPOSITION II

A new process for recovering hydrogen fluoride (HF) from aqueous fluosilicic acid (H_2SiF_6) solutions is proposed. The novel step of this process consists of contacting a H_2SiF_6 solution with a hydrate forming compound to separate the water as a hydrate.

Introduction

In the acidulation and thermal processing of phosphate ores gaseous hydrogen fluoride and silicon tetrafluoride are evolved. These gases are recovered by absorption in water and react to form fluosilicic acid :

$$2\,HF + SiF_4 \rightleftharpoons H_2SiF_6 \qquad (1)$$

$$3\,SiF_4 + 2\,H_2O \rightleftharpoons 2\,H_2SiF_6 + SiO_2 \qquad (2)$$

$$6\,HF + SiO_2 \rightleftharpoons H_2SiF_6 + 2\,H_2O \qquad (3)$$

Solutions containing 25-30% H_2SiF_6 can be obtained (1). Fluosilicates such as sodium fluosilicate can be precipitated directly by the addition of the appropriate salt. Unfortunately the market for fluosilicates is relatively small and in most phosphate operations fluosilicic acid is an undesirable by-product. Recently a new process was developed to make aluminum fluoride from fluosilicic acid solutions (2).

Kirk and Othmer (1) state that "fluosilicic acid solutions are not conveniently convertible to hydrogen fluoride by known processes". In January 1962 Stauffer Chemical Company (3) claimed to have developed a commercially feasible continuous process for producing anhydrous hydrogen fluoride from fluosilicic acid, but no details were published.

J. C. Porter made a study of this problem and has reported his findings in "Study of the Recovery of Hydrofluoric Acid from Fluosilicic Acid", Chemical Engineering Laboratory, C.I.T., Dec.'62.

Proposed Process

Fluosilicic acid, like carbonic acid, only exists in solution. The vapor-liquid equilibrium diagram for the system $H_2 Si F_6$ - HF-H_2O at one atmosphere has been determined (4) and is shown in Figure 1. It is apparent that distillation of a 25-30% $H_2 Si F_6$ solution results in a ternary azeotrope at 116°C with a composition of 36% $H_2 Si F_6$, 10% HF and 54% water.

It is proposed that if the azeotropic liquid were cooled down and dehydrated by adding a hydrate forming compound, the solution would become saturated and gaseous HF and $Si F_4$ would be evolved as the dehydration continued. It is proposed that the gaseous hydrating agent technique used in saline water conversion may be applied here.

To determine the feasibility of the process, equilibrium and rate data would have to be determined. The operating conditions depend on the choice of hydrating agent. Many compounds form hydrates (5). Propane has a satisfactory rate of hydrate formation (6) and is inexpensive. A flow diagram based on propane is given in Figure 2.

The feed is concentrated to the azeotropic composition and then cooled and contacted with liquid propane. Propane serves a double role as hydrate forming substance and internal direct cooling medium. Gaseous HF, $Si\ F_4$ and $C_3\ H_8$ will be evolved. The propane hydrate crystals are filtered off and the filtrate is heated up to flash off some more HF and $Si\ F_4$ and is then recycled to the reactor. The combined reactor and flasher vapors are separated by fractionation into product HF, liquid $C_3\ H_8$ recycle and $Si\ F_4$. The hydrate crystals are melted to produce water and liquid $C_3\ H_8$ recycle. In the saline water conversion process (6) the hydrate is formed at 35°F and 57 psig and melted at 45°F and 70 psig. This gives some idea of the magnitude of the required operating conditions. As indicated by Equation (2), it might be possible to recycle the $Si\ F_4$ gas to produce more $H_2\ Si\ F_6$.

References

1. Kirk, R. E., Othmer, P. F., Editors,
Encyclopedia of Chemical Technology, 6, 703, 725-7
The Interscience Encyclopedia, Inc., New York (1951)
2. Weinrotter, F., Chem. Eng., V.71, No.9, 132 (April 27, 1964)
3. "Research and Technology Concentrates", Chem. Eng. News,
p.43, (Jan. 8, 1962)
4. Munter, P. A., et al, Ind. Eng. Chem., 39, 427 (1947)
5. Pauling, Linus, Science, V.134, No.3471, p.15, (July 7,1961)
6. Knox, W. G., et al, Chem. Eng. Progress, V.57, No.2
p.66, (1961)

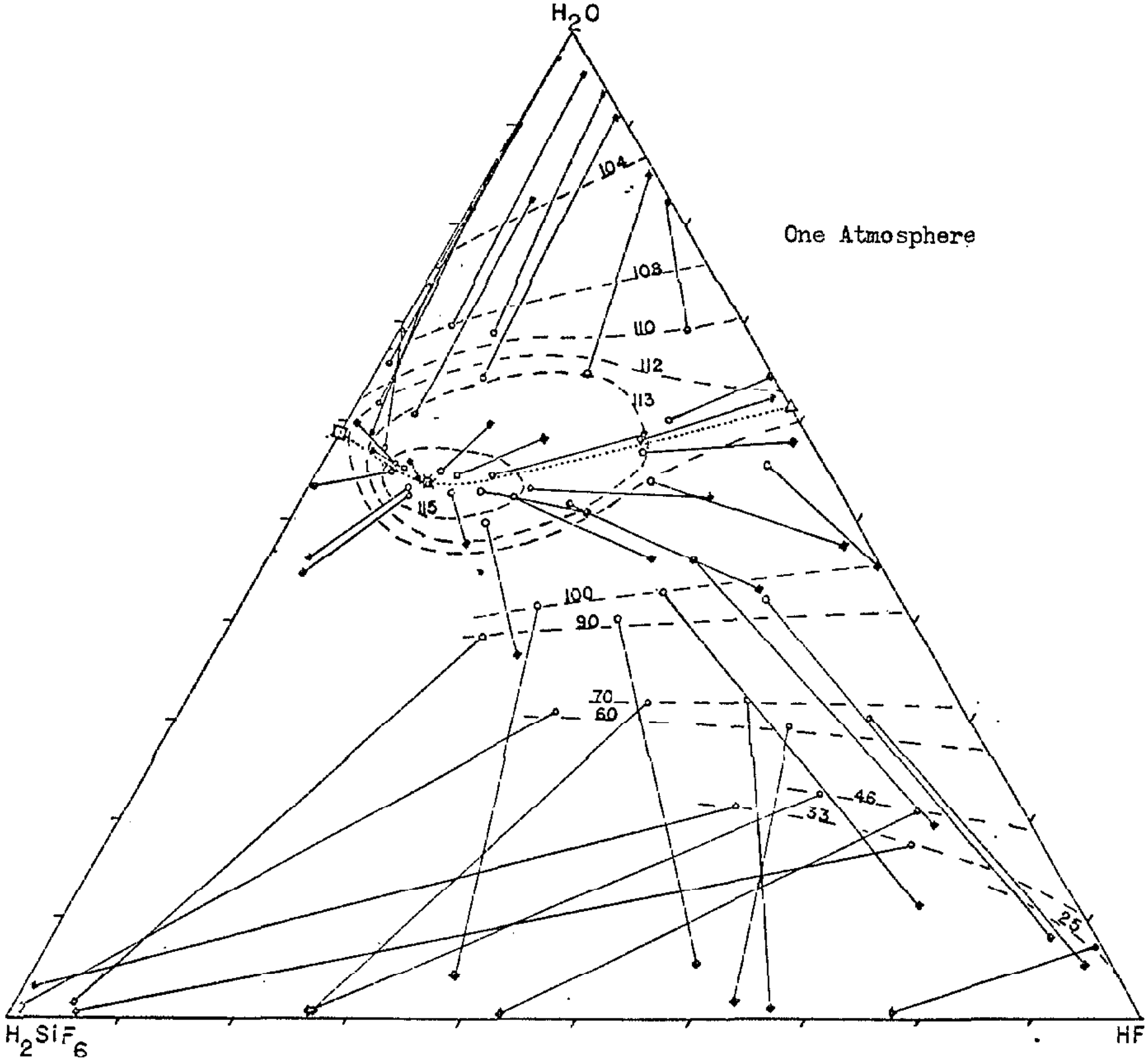

Figure 7. Liquid-Vapor Equilibria Diagram for System HF-H_2SiF_6-H_2O

- * Ternary constant boiling point
- ○ Liquid composition, weight %
- ◆ Vapor composition, weight %
- — Tie lines
- — — — Liquid isotherms
- .... Vapor pressure trough
- △ Constant boiling point of system HF-H_2O
- □ Approximate constant boiling point of system H_2SiF_6-H_2O

Figure 1

Courtesy of Ind. & Eng. Chem. I.E.C. 39, 427 (1947)

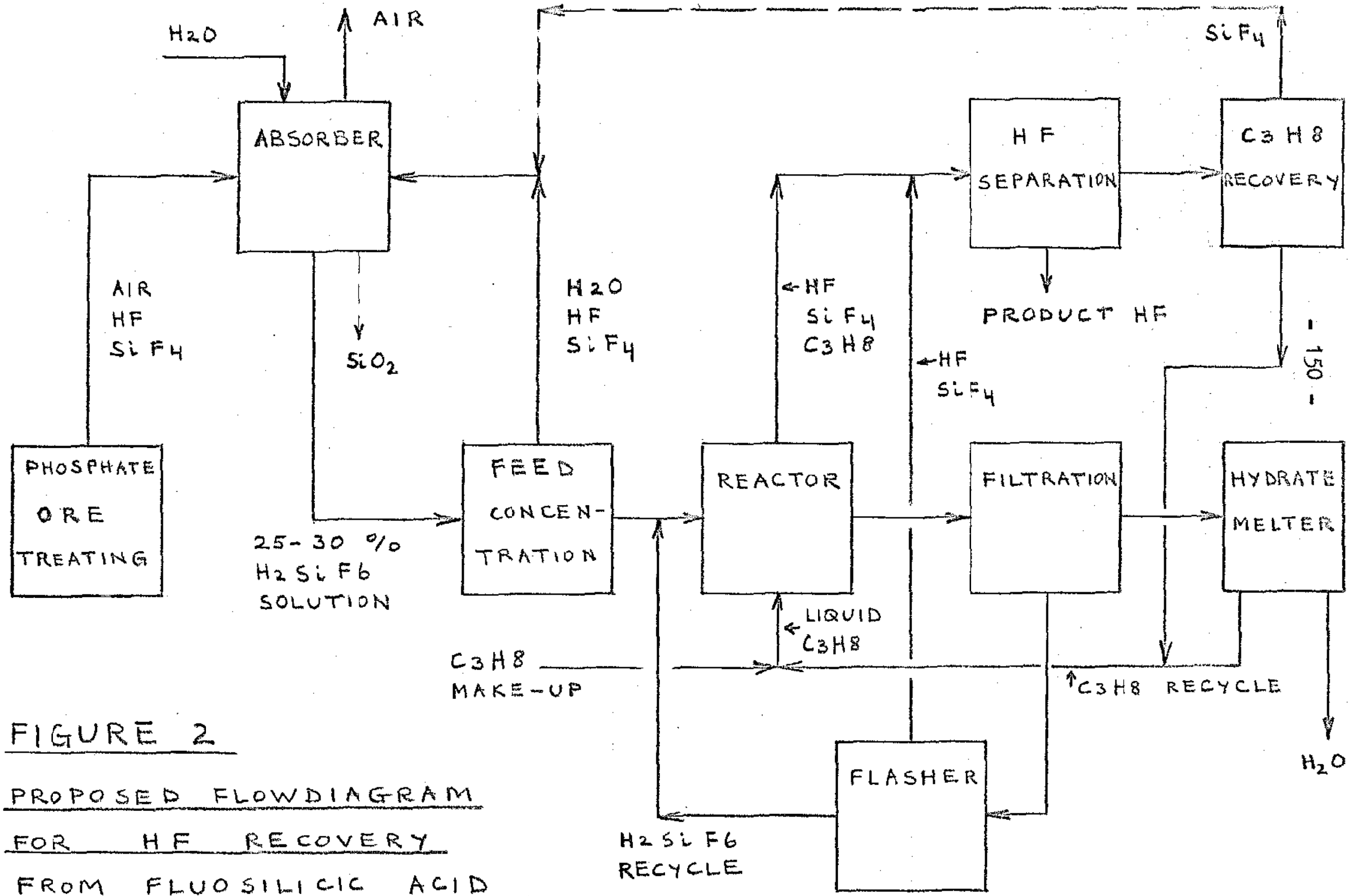

FIGURE 2

PROPOSED FLOWDIAGRAM
FOR HF RECOVERY
FROM FLUOSILICIC ACID

PROPOSITION III

A process to separate pure hydrogen fluoride (HF) from aqueous fluosilicic acid ($H_2\,Si\,F_6$) solutions is proposed. Information in the literature indicates that the azeotropic composition of fluosilicic acid solutions shifts from 41% $H_2\,Si\,F_6$ at 115.5°C. and one atmosphere to 60% $H_2\,Si\,F_6$ at 21°C under vacuum. This will enable separation of pure HF by straight fractionation processes.

Introduction

See introduction of Proposition II

Discussion

The fluosilicic acid-water system exhibits azeotropic behavior in the form of a constant boiling-point mixture at a liquid composition of 41 weight per cent $H_2\,Si\,F_6$ at 115.5°C and one atmosphere (1). This is indicated in Figure 1 (of Proposition II).

Jacobson (2) concentrated an aqueous $H_2\,Si\,F_6$ solution from 25 to 41% $H_2\,Si\,F_6$ by distillation under diminished pressure at 21°C by admitting a tiny stream of air into the distilling liquid. Further concentration of the 41% solution was accomplished by vacuum distillation at 21°C. When the liquid concentration had reached 54% $H_2\,Si\,F_6$ the distillate contained 1.5% $H_2\,Si\,F_6$. A maximum concentration of 60% $H_2\,Si\,F_6$ was obtained on further distillation and it appeared that this was close to the azeotropic concentration. A 54-60% $H_2\,Si\,F_6$

solution at one atmosphere is "on the other side" of the 41% azeotropic composition when compared with a 25% $H_2 Si F_6$ solution. It is apparent that fractionation of a 54-60% $H_2 Si F_6$ solution at one atmosphere will enable separation into a pure $H_2 Si F_6$ overhead and a constant boiling bottoms product. Since pure $H_2 Si F_6$ cannot exist, the overhead product will be in the form of hydrogen fluoride (HF) and silicon tetrafluoride ($Si F_4$). The boiling points of HF (19.4°C) and $Si F_4$ (-65.0°C) indicate that these compounds can be easily separated by fractionation. There is no indication in the literature that these two compounds might form an azeotrope.

At one atmosphere the vapor above a 25% $H_2 Si F_6$ bubble-point liquid has a higher $Si F_4/HF$ ratio than the liquid. Distillation of a 25% $H_2 Si F_6$ solution at one atmosphere will therefore produce a solution containing free HF. Figure 1 (of Proposition II) shows that a ternary azeotrope results with a boiling point of 116°C and a composition of 36% $H_2 Si F_6$, 10% HF and 54% water. No free HF is formed during distillation under vacuum at 21°C (2). The water content of the ternary azeotropic solution can be further reduced by vacuum distillation at 21°C to bring the solution "on the other side" of the atmospheric azeotropic composition.

A flow diagram of the proposed process is given in Figure 1. The feed is concentrated to the azeotropic composition at one atmosphere. The vacuum tower decreases the water content to somewhere between 46 and 40% H_2O and operates at room temperature. The concentrated solution is then pumped to the atmospheric tower where the bottoms temperature is maintained at the azeotropic boiling point for one atmosphere. The bottoms product is recycled to the vacuum tower. The overhead product of the atmospheric tower is separated into pure HF and $Si\ F_4$ by fractionation . The $Si\ F_4$ may be recycled to the absorber to produce more HF.

The technical feasibility of this process will depend to a great extent on the rate of water removal that can be obtained in the vacuum tower. The partial pressure of water for strong $H_2\ Si\ F_6$ solutions is small. A Russian reference (3) (translation in (4)), indicates that at 50°C a 46% $H_2\ Si\ F_6$ solution has a water partial pressure of 50 mm mercury. Since the vapor pressure at this temperature is 91 mm the partial pressure is about half the vapor pressure. Applying this to 21°C , it appears that the vapor pressure would be of the order of 10 mm mercury. The above reasoning was for a 46% $H_2\ Si\ F_6$ concentration and at higher concentrations the water partial pressure will be even lower. The vaporization will probably be diffusion controlled and a large surface area of the liquid is desirable. A packed column with liquid recirculation seems an appropriate choice for the vacuum tower.

One way to increase the partial pressure driving force is to increase the temperature. Reference (3) shows that for a 46% $H_2\ Si\ F_6$ solution the partial pressures of $Si\ F_4$ and HF are extremely small at 50°C. The volatility of these components would therefore not interfere with operating at 50°C. However, the azeotrope concentration will decrease with an increase in temperature and this will put an upper limit on the operating temperature. The optimum temperature is probably somewhere between 20 and 50°C.

References

1. Munter, P. A., et al, "Hydrofluoric Acid-Water and Hydrofluoric Acid-Hydrofluosilicic Acid-Water", Ind. Eng. Chem., 39, p.427-31 (1947)
2. Jacobson, C. A., J. Phys. Chem., 27, 577-80, 762-70 (1923)
3. Yatlov, V. S., Pineavskaya, E. N., J. Applied Chem (U.S.S.R.) 14, 11-13 (1941)
4. Porter, J. C., "Study of Recovery of Hydrofluoric Acid from Fuosilicic Acid", Chem. Eng. Dept., Student Report, C.I.T. (1962)

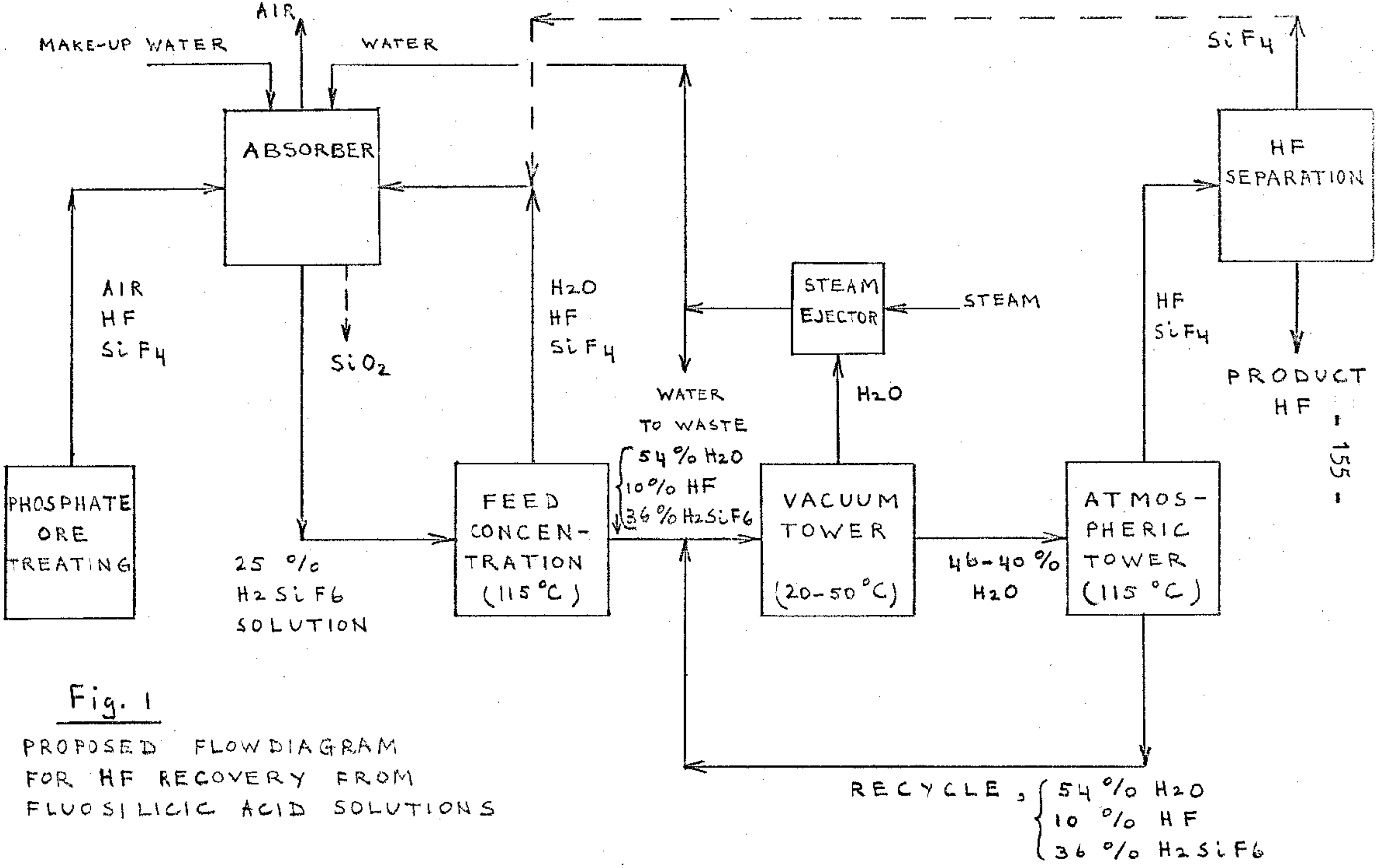

Fig. 1

PROPOSED FLOWDIAGRAM FOR HF RECOVERY FROM FLUOSILICIC ACID SOLUTIONS

PROPOSITION IV

A recently published method for estimating enthalpies of hydrocarbon mixtures at the bubble-point state may be improved by making a correction for the heat of mixing.

Introduction

Stevens and Thodos (1) have published a method to estimate the enthalpies of hydrocarbon mixtures at their saturated vapor and liquid states. The method consists of determining the enthalpy of the mixture at zero pressure at a given temperature by adding the pure component vapor enthalpies. The enthalpy of the mixture at dew point and at bubble point is then determined by making corrections for the effect of pressure on enthalpy. These corrections are expressed as functions of the pseudocritical compressibility factor, the pseudocritical temperature, and the temperature.

Discussion

In principle it is possible to make enthalpy pressure-corrections at constant temperature and constant composition from generalized volumetric data. This method works fairly well in the vapor phase and dew-point vapor enthalpies can be predicted with some degree of accuracy. In order to obtain the difference in enthalpy of the mixture at the dew-point and bubble-point states the following integral must be evaluated :

$$H_d - H_b = -\int_{P_d}^{P_b} \left\{ V - T \left(\frac{\partial V}{\partial T}\right)_{P,n} \right\}'' dP'' \qquad (1)$$

where V represents the specific volume of the total mixture in the two-phase region. The composition and amount of both the vapor and liquid phase change from dew-point pressure to bubble-point pressure. The author considers it doubtful whether such integrals can be accurately presented as a general expression in terms of the pseudocritical compressibility factor and the pseudocritical temperature. Another point to consider is that on mixing hydrocarbon liquids the volume change is often very small while there may be a considerable heat of mixing.

It is proposed that the correlation of Stevens and Thodos may be improved by adding an additional generalized correction term for the heat of mixing in the liquid phase. A generalized correlation for the heat of mixing of binary paraffin mixtures has been established. Brønsted and Koefoed (2) have called this relation the "principle of congruence". The heat of mixing (or excess enthalpy) may be correlated as

$$H^E = B \left(n_1 - n_2\right)^2 x_1 x_2 \qquad (2)$$

where

H^E = difference between the enthalpy of the mixture and the sum of the enthalpies of the pure components at the same temperature and pressure, Btu/mole

B = a function of temperature only.

n_1, n_2 = number of carbon atoms in each component

x_1, x_2 = mole fractions of the components

The principle is primarily an empirical observation, but Longuet-Higgins (3) has derived it for a statistical model of long-chain molecules. The dependence of B on temperature has only been established for a few systems. It is known that B decreases with increasing temperature and eventually becomes negative (4). Recently Lündberg (5) at Shell Development Company has started a systematic experimental program to measure heats of mixing for hydrocarbons. The results for 27 binary hydrocarbon systems at 25° and 50°C have been published (5). Adcock and McGlashan (6) have correlated the heat of mixing for carbon-tetrachloride and cyclo-hexane as a function of temperature by the relation

$$H^E = x_1 x_2 \left(C - D T \right) \tag{3}$$

where C and D are constants. It is apparent that at high values of the temperature T the excess enthalpy can become negative. It is therefore suggested that the constant B may be correlated as a function of temperature by an equation of the form

$$B = C' - D' T \tag{4}$$

The discussion so far has only been applicable to binary mixtures. It is proposed that a multicomponent mixture be treated as a pseudobinary mixture. Split the multicomponent mixture in two equal mole fractions, one section containing the light components and the other half containing the heavy components. The average molar number of carbon atoms can then be determined for each half of the mixture.

It should be noted that the estimation of enthalpies of mixtures is a problem that is not yet solved, although a considerable amount of work has been done on the subject, both by physical chemists (7) and chemical engineers (8). The suggestions made so far should therefore be considered as possible approaches rather than solutions to the problem.

References

1. Stevens, W. F., Thodos, George, A. I. Ch.E. Journal, Vol. 9, No. 3, p.293 (1963)
2. Rowlinson, J. S., "Liquids and Liquid Mixtures", p.146, Academic Press Inc., London (1959)
3. Longuet-Higgins, H. C., Disc. Faraday Soc., 15, 73 (1953)
4. Ref. 2, p.143, 145, 146, 147, 150
5. Lundberg, G. W., J. Chem. Eng. Data, 9, 193 (1964)
6. Ref. 2, p.151
7. Hildebrand, J. H., Scott, R. L., "Regular Solutions", Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962
8. "Applied Thermodynamics", Chem. Eng. Progress Symposium Series, No. 7, Vol. 49, 1953, A.I.Ch.E. New York

PROPOSITION V

Partial enthalpy changes upon vaporization for the components of the dioxane-water system have been published. It is proposed that the method used to obtain these results is not correct.

Introduction

Stallard and Amis (1) carried out the following investigation : A stream of dry air was passed through a mixture of dioxane and water in a calorimeter. Electrical energy was supplied to keep the temperature constant at 40°C. The vaporized material was condensed and its composition determined. The total pressure was essentially constant at one atmosphere. A plot of the heat of vaporization per unit weight of vapor versus liquid composition produced a curve with the shape of a horizontal integral sign. The "partial specific heats of vaporization" for water and dioxane were determined by drawing tangents to this curve and finding the intercepts of the tangents on the 100% water and 100% dioxane ordinates respectively. Large negative values were obtained for the "partial specific heat of vaporization" of dioxane at liquid compositions below 20% dioxane. The results were checked by the relation

$$\overline{\lambda}_H \, x_H + \overline{\lambda}_D \, x_D = \lambda \qquad (1)$$

where λ represents the heat of vaporization.

It is proposed that this method of determining the "partial specific heats of vaporization" for the components is not correct.

Discussion

The "specific heat of vaporization" measured by Stallard and Amis can be represented as $\sum_{k=1}^{2} (\bar{H}_{k,g} - \bar{H}_{k,l})y_k$, where the partial enthalpies are to be taken at the conditions of the test, i.e. 40°C and one atmosphere. The total pressure of one atmosphere was much higher than the bubble-point pressure at 40°C. If it is assumed that

a The effect of pressure on the partial enthalpies in the liquid and in the gas phase is negligible

b The higher total pressure and the presence of air do not change the concentrations of the components in the vapor phase

then the measured quantity will be the same as the enthalpy change upon vaporization discussed in Part III of the Thesis. It is apparent that x_H and x_D in Equation (1) should be y_H and y_D since the vaporized material has the composition of the vapor. The meaning of the slope of a plot of $\sum_{k=1}^{2} (\bar{H}_{k,g} - \bar{H}_{k,l})y_k$ versus x_k and y_k will now be discussed.

Let the two components of the binary system be j and k. Differentiation of the quantity $\sum_{k=1}^{2}(\bar{H}_{k,g}-\bar{H}_{k,l})y_k$ results in

$$d\left\{(\bar{H}_{k,g}-\bar{H}_{k,\ell})\,y_k+(\bar{H}_{j,g}-\bar{H}_{j,\ell})\,y_j\right\}=$$

$$\left\{(\bar{H}_{k,g}-\bar{H}_{k,\ell})-(\bar{H}_{j,g}-\bar{H}_{j,\ell})\right\}dy_k$$

$$+\left(y_k\,d\bar{H}_{k,g}+y_j\,d\bar{H}_{j,g}\right)$$

$$-\left(y_k\,d\bar{H}_{k,\ell}+y_j\,d\bar{H}_{j,\ell}\right) \tag{2}$$

The partial enthalpies can be considered to be a function of P, T, and the weight fraction n_k of component k :

$$d\bar{H}_k=\left(\frac{\partial\bar{H}_k}{\partial T}\right)_{P,n}dT+\left(\frac{\partial\bar{H}_k}{\partial P}\right)_{T,n}dP+\left(\frac{\partial\bar{H}_k}{\partial n_k}\right)_{P,T}dn_k \tag{3}$$

The Gibbs-Duhem equation may be written as

$$y_k \left(\frac{\partial \bar{H}_{k,g}}{\partial y_k}\right)_{P,T} + y_j \left(\frac{\partial \bar{H}_{j,g}}{\partial y_k}\right)_{P,T} = 0 \qquad (4)$$

and

$$x_k \left(\frac{\partial \bar{H}_{k,\ell}}{\partial x_k}\right)_{P,T} + x_j \left(\frac{\partial \bar{H}_{j,\ell}}{\partial x_k}\right)_{P,T} = 0 \qquad (5)$$

By combining Equations (2), (3), (4) and (5) for the case of constant temperature the following general expression is obtained:

$$\begin{aligned} d \left[\sum_{k=1}^{2} \left(\bar{H}_{k,g} - \bar{H}_{k,\ell} \right) y_k \right]_T = \\ & \left\{ \left(\bar{H}_{k,g} - \bar{H}_{k,\ell} \right) - \left(\bar{H}_{j,g} - \bar{H}_{j,\ell} \right) \right\} dy_k \\ & + \left[\left\{ y_k \left(\frac{\partial \bar{H}_{k,g}}{\partial P}\right)_{T,y} + y_j \left(\frac{\partial \bar{H}_{j,g}}{\partial P}\right)_{T,y} \right\} \right. \\ & \left. - \left\{ y_k \left(\frac{\partial \bar{H}_{k,\ell}}{\partial P}\right)_{T,x} + y_j \left(\frac{\partial \bar{H}_{j,\ell}}{\partial P}\right)_{T,x} \right\} \right] dP \qquad (6) \\ & - \left(\frac{y_k - x_k}{1 - x_k} \right) \left(\frac{\partial \bar{H}_{k,\ell}}{\partial x_k} \right)_{P,T} dx_k \end{aligned}$$

If we now apply Equation (6) to the case of Stallard and Amis at constant temperature and constant pressure the following result is obtained

$$\left\{ d \left(\sum_{k=1}^{2} (\bar{H}_{k,g} - \bar{H}_{k,l}) y_k \middle/ d x_k \right\}_{T,P} \right. =$$

$$\left\{ (\bar{H}_{k,g} - \bar{H}_{k,l}) - (\bar{H}_{j,g} - \bar{H}_{j,l}) \right\} \left(\frac{d y_k}{d x_k} \right)_{P,T}$$

$$- \left(\frac{y_k - x_k}{1 - x_k} \right) \left(\frac{\partial \bar{H}_{k,l}}{\partial x_k} \right)_{P,T} \tag{7}$$

From the general properties of partial quantities we know that

$$\left\{ d \left(\sum_{k=1}^{2} \bar{G}_k \, n_k \right) / d n_k \right\}_{P,T} = \bar{G}_k - \bar{G}_j \tag{8}$$

It is apparent that the intercepts of the tangent to the plot of $\sum_{k=1}^{2} (\bar{H}_{k,g} - \bar{H}_{k,l}) y_k$ versus x_k do not correspond to the partial enthalpy changes upon vaporization.

Intuitively one might expect that a plot of $\sum_{k=1}^{2} (\bar{H}_{k,g} - \bar{H}_{k,l}) y_k$ versus y_k at constant P and T would yield the partial enthalpy changes upon vaporization for the components. The slope of the curve for this case can be expressed as

$$\left\{ d\left(\sum_{k=1}^{2} (\bar{H}_{k,g} - \bar{H}_{k,\ell})\, y_k \right) \Big/ d y_k \right\}_{T,P} =$$

$$\left\{ (\bar{H}_{k,g} - \bar{H}_{k,\ell}) - (\bar{H}_{j,g} - \bar{H}_{j,\ell}) \right\}$$

$$- \left(\frac{y_k - x_k}{1 - x_k} \right) \left(\frac{\partial \bar{H}_{k,\ell}}{\partial x_k} \right)_{P,T} \left(\frac{d x_k}{d y_k} \right)_{T,P} \qquad (9)$$

For an ideal solution the term

$$\left(\partial \bar{H}_{k,\ell} / \partial x_k \right)_{P,T} = 0 \qquad (10)$$

Thus only for an ideal solution do the intercepts of the tangent to the curve of $\sum_{k=1}^{2} (\bar{H}_{k,g} - \bar{H}_{k,1})y_k$ versus y_k represent the partial enthalpy changes upon vaporization for the components. It can be concluded therefore that it is not possible to obtain the partial enthalpy changes upon vaporization from an isothermal plot of the enthalpy change upon vaporization $\sum_{k=1}^{2} (\bar{H}_{k,g} - \bar{H}_{k,1})y_k$ versus either y_k or x_k. This holds even when both temperature and pressure are constant.

Reference

1. Stallard, R. D., Amis, E. S., J. Am. Chem. Soc., 74, 1781(1952)

Nomenclature

Symbols

G	an external thermodynamic property
H	enthalpy, Btu/lb
n	weight fraction
P	pressure, psia
T	temperature, °R
x	weight fraction in liquid
y	weight fraction in gas
λ	specific heat of vaporization, Btu/lb

Subscripts

D	dioxane
g	gas
H	water
j	component j
k	component k
l	liquid

Superscripts

$\overline{\ }$	partial value