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A SIMPLE METHOD FOR LIQUID ENTHALPY DEPARTURE CALCULATIONS

BY

CHING-LIN CHIEN

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

AT

NEWARK COLLEGE OF ENGINEERING

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Newark, New Jersey
1971

APPROVAL OF THESIS

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BY

CHING-LIN CHIEN

FOR

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NEWARK COLLEGE OF ENGINEERING

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FACULTY COMMITTEE

APPROVED: _____

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SEPTEMBER, 1971

Abstract

The reduced equation of state for gases and liquids developed by Benson and Golding in 1951 is modified and used to calculate liquid enthalpy departures for saturated pure substances and mixtures. The temperature-independent coefficients in the modified equation are determined from critical properties and experimental liquid enthalpies at the boiling point and at the critical point. The results of the proposed method are compared with those predicted with the modified Redlich-Kwong equation of state by Joffe and Zudkevitch.

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Introduction

The enthalpy of a saturated liquid at any given temperature can be obtained from the enthalpy departure evaluated analytically using an equation of state such as the Redlich-Kwong equation with the two coefficients, a and b , treated as temperature-dependent variables (1).

The method applied in this study has its origin in the modified Van der Waals equation developed by S. W. Benson and E. Gerjuoy in 1950 (2) :

$$P = RT / (V - bV^{-s}T^{-n}) - a / (V^m T^p) \quad (1)$$

The various exponents in the equation were evaluated by Benson and R.

A. Golding (3) based on the following criteria:

- (a) Trouton's rule: $\text{Evap}/RT = 9.5$ (at the boiling point)
- (b) Critical ratio: $1/Z_C = RT_C/P_C V_C = 3.70$
- (c) Liquid density rule: $1/\rho_b = 2.72$ (at the boiling point)
- (d) The coefficients of thermal expansion and compressibility at normal boiling points are about $1.3 \times 10^{-3}/^\circ\text{K}$ and $1.5 \times 10^{-4}/\text{atmos.}$ respectively.

The equation with the best choice of exponents becomes:

$$P = RT / (V - bV^{-\frac{1}{2}}) - a / (V^{\frac{5}{3}} T^{\frac{2}{3}}) \quad (2)$$

where $a = 0.9099 RT_C^{\frac{5}{3}} V_C^{\frac{5}{3}}$ (2a)

$$b = 0.1567 V_C^{\frac{1}{2}} \quad (2b)$$

and in reduced form:

$$\frac{P}{P_c} = \pi = 3.624 \left(\theta / (\theta - 0.1567 \theta^{-1}) - 0.9099 / (\theta^{\frac{5}{3}} \theta^{\frac{2}{3}}) \right) \quad (3)$$

where $\theta = V/V_c$; $\theta = T/T_c$.

It is shown by Benson and Golding (3) that this equation in predicting some physical properties such as liquid densities of non-associated substances, heats of vaporization and gas isotherms gives better results than the Van der Waals and Berthelot equations.

In the current study Equation 2 was applied to the calculation of liquid enthalpy departures of non-polar substances and mixtures. The systems studied were methane, propane, nitrogen, carbon dioxide and methane-propane mixtures. Satisfactory results were obtained with some modifications of the equation. A polar compound, ammonia, was also investigated.

Pure Substances

Liquid enthalpy departure can be calculated using the following thermodynamic relations:

$$(H^* - H)_T = RT - PV + \int_{\infty}^V (P - T(\partial P/\partial T)_V) dV \quad (4)$$

Differentiating Equation 2,

$$(\partial P/\partial T)_V = R/(V - bV^{-\frac{1}{2}}) + 2a/(3V^{\frac{5}{3}}T^{\frac{2}{3}}) \quad (5)$$

Multiplying both sides by T,

$$T(\partial P/\partial T)_V = RT/(V - bV^{-\frac{1}{2}}) + 2a/(3V^{\frac{5}{3}}T^{\frac{2}{3}}) \quad (6)$$

Substituting Equations 2 and 6 into Equation 4:

$$\begin{aligned} (H^* - H)_T &= RT - PV + \int_{\infty}^V (RT/(V - bV^{-\frac{1}{2}}) - a/(V^{\frac{5}{3}}T^{\frac{2}{3}}) \\ &\quad - RT/(V - bV^{-\frac{1}{2}}) - 2a/(3V^{\frac{5}{3}}T^{\frac{2}{3}})) dV \\ &= RT - PV - \int_{\infty}^V (5a/(3V^{\frac{5}{3}}T^{\frac{2}{3}})) dV \\ (H^* - H)_T &= RT - PV + 5a/(2V^{\frac{2}{3}}T^{\frac{2}{3}}) \end{aligned} \quad (7)$$

where P and T are given, V is calculated from Equation 2 with the constants a and b evaluated from Equations 2a and 2b. Results obtained from Equation 7 for saturated liquid methane, propane, nitrogen and carbon dioxide were compared in the current study with the experimental values (4) and were found to be of low accuracy.

One of the original criteria used by Benson and Golding, the critical ratio, $1/Z_C$, has a generalized value of 3.70, or $Z_C = 0.270$. Since the

critical compressibility factors of most compounds are different from 0.270 (5), one of the exponents was changed in the current study to fit the experimental critical compressibility factor. The modified equation

$$P = RT/(V - bV^{-\frac{1}{2}}) - a/(V^n T^{\frac{3}{2}}) \quad (8)$$

where $a = C_1 RT_c^{3/2} V_c^{n-1}$ and $b = C_2 V_c^{3/2}$, was made to satisfy the following conditions:

$$P_c = RT_c/(V_c - bV_c^{-\frac{1}{2}}) - a/V_c^n T_c^{3/2} = Z_c RT_c/V_c \quad (9)$$

$$(\partial P/\partial V)_{c.p.} = (-RT_c)(1 + \frac{1}{2}bV_c^{-\frac{3}{2}})/(V_c - bV_c^{-\frac{1}{2}})^2 + a n V_c^{-n-1} T_c^{-\frac{3}{2}} = 0 \quad (10)$$

$$(\partial^2 P/\partial V^2)_{c.p.} = 3RT_c b V_c^{-\frac{5}{2}} / (4(V_c - bV_c^{-\frac{1}{2}})^2) + 2RT_c(1 + \frac{1}{2}bV_c^{-\frac{3}{2}})^2 / (V_c - bV_c^{-\frac{1}{2}})^3 - a(n+1)V_c^{-n-2} T_c^{-\frac{3}{2}} = 0 \quad (11)$$

By substituting a and b as defined for Equation 8 into Equations 9, 10, and 11, the constants C_1 , C_2 and n can be calculated. The results are listed in Table 1.

Table 1

Constants Used in Equation 8

	Z	C	C	n
CH ₄	0.290	0.910	0.1667	1.715
C ₃ H ₈	0.277	0.910	0.1575	1.670
N ₂	0.291	0.909	0.1670	1.716
CO ₂	0.2745	0.910	0.1558	1.662

The enthalpy departure can be calculated with the following equation:

$$(H^* - H)_T = RT - PV + 5a/(3(n-1)V^{n-1}T^{2/3}) \quad (12)$$

The above change did not show any substantial improvement in accuracy over Equation 7.

Another trial was carried out by changing another exponent:

$$P = RT/(V - bV^{-m}) - a/(V^3 T^{2/3}) \quad (13)$$

where $a = C_3 R T_c^{5/3} V_c^{2/3}$ and $b = C_4 V_c^{m+1}$

Again, the three conditions at the critical point used before were applied and C_3 , C_4 and m were evaluated. This attempt was likewise unsuccessful, since the change of the exponent of the volume in the first term of the equation has almost no effect on the enthalpy departure.

From the previously calculated results, it was apparent that the deviation from the experimental value becomes larger as the temperature comes closer to the boiling point. Therefore, two exponents were changed to fit the vapor pressure and liquid density data at the boiling point in addition to the three conditions at the critical point:

$$P = RT/(V - bV^{-1}) - a/(V^n T^m) \quad (14)$$

where $a = C_5 R T_c^{m-1} V_c^{n-1}$ and $b = C_6 V_c^{3/2}$; and the enthalpy departure becomes:

$$(H^* - H)_T = RT - PV + (m+1)a/((n-1)V^{m-1}T^{n-1}) \quad (15)$$

This modification did not improve the results significantly. However, from the previous attempts, it was found that the temperature exponent has a greater effect on enthalpy departure than the volume exponent, and that the temperature-enthalpy profile is of an inverse exponential type. Since $e^{-x} = 1 - x/1! + x^2/2! - x^3/3! + \dots$, the exponential can be approximated by omitting the terms after the second one. In order to compensate for the terms omitted, an exponent was added to the second term and a modified temperature function, $(a - dT^m)$, was tried:

$$P = RT/(V - bV^{-\frac{1}{2}}) - (a - dT^m)/V^n \quad (16)$$

$$\text{where } a = C_7 RT_c V_c^{n-1} \quad (16a)$$

$$b = C_8 V_c^{\frac{3}{2}} \quad (16b)$$

$$d = C_9 RT_c^{1-m} V_c^{n-1} \quad (16c)$$

Applying the three conditions of Equations 9, 10 and 11, there is obtained for the enthalpy departure:

$$(H^* - H)_T = RT - PV + (a + (m - 1)dT^m)/((n - 1)V^{n-1}) \quad (17)$$

The three conditions at the critical point and the experimental liquid enthalpies at the boiling point and at the critical point were used to determine C_7 , C_8 , C_9 , n and m for each of the pure substances studied. The polar substance, ammonia, was added to those previously studied. The values are given in Table 2.

To find the enthalpy departure with Equation 17, the following procedure is used: the temperature and vapor pressure of the pure substance are substituted into Equation 16 and the latter is solved for

the liquid volume. The calculated liquid volume is substituted into Equation 17 to obtain the enthalpy departure.

The calculated enthalpy departures are compared with the experimental values as shown in Tables 3-7.

Table 2

Constants Used in Equation 16

	C ₇	C ₈	C ₉	n	m
CH ₄	2.250	0.1667	1.340	1.715	0.385
C ₃ H ₈	3.680	0.1575	2.770	1.670	0.250
N ₂	2.340	0.1670	1.431	1.716	0.385
CO ₂	3.580	0.1558	2.670	1.662	0.300
NH ₃	3.490	0.1342	2.577	1.559	0.270

Binary Mixtures

The methane-propane system of three different compositions, 76.6 5.2 and 12 mole per cent propane-in-methane mixtures, were studied using the proposed method.

The enthalpy departure of each component was calculated at a reduced temperature which is the same as the pseudoreduced temperature of the mixture. The latter is defined as the temperature of the mixture divided by the pseudocritical temperature. The pseudocritical temperature can be established by applying a mixing rule. Two mixing rules were used: Kay's rule (6) and the correlation developed by Yesavage and Powers (7).

The enthalpy departure of the mixture was found as the summation of the enthalpy departures of each component calculated as explained above and multiplied by its mole fraction in the mixture. This procedure for finding a residual property of a mixture has been discussed elsewhere by Joffe (11).

The results are presented in Table 8 along with the experimental values (8,9,10) and the calculations of Joffe and Zudkevitch who used the modified Redlich-Kwong Equation of State with temperature-dependent coefficients (1).

Discussion of Results

The proposed method with the temperature-independent coefficients derived from the Equation of State of Benson and Golding predicts the liquid enthalpy departures in close agreement with the experimental values for the four non-polar, pure substances tested. The maximum absolute deviation is 3.3 Btu/lb (Tables 3 to 6). It also works reasonably well for the non-polar mixtures tested in this study, provided that the proper mixing rule is applied (Table 8). The average deviation of the calculated values is of the same order of magnitude as for the method of Joffe and Zudkevitch.

For the polar substance, liquid ammonia, the calculated enthalpy departure and the experimental value are fairly close at temperatures near the boiling point and the critical point (Table 7). For the temperature range from 280°K to 380°K, the average absolute deviation is approximately 14.9 Btu/lb and the maximum deviation is about 20.6 Btu/lb. This is probably the result of the difference in the temperature-enthalpy profiles for non-polar and polar substances. One possible correction for this deviation is to add another temperature term to the existing ($a - dT^m$) function presently employed. Another possible solution is to make the exponent m , a temperature-dependent one. This will make the enthalpy departure expression very complicated.

Table 3

Enthalpy Departures of Saturated Liquid Methane

Temperature in °K	Pressure in Atm	$H^* - H_f$, Btu/lb	
		Experimental	Calculated
120	1.905	217.5	214.5
125	2.669	214.3	211.8
130	3.641	211.0	209.0
135	4.855	207.5	206.0
140	6.339	203.9	202.8
145	8.132	200.0	199.3
150	10.27	196.0	195.6
155	12.79	191.6	191.6
160	15.74	186.9	187.1
165	19.14	181.8	182.1
170	23.00	176.0	176.3
175	27.49	169.5	169.6
Average absolute deviation			1.0

Table 4

Enthalpy Departures of Saturated Liquid Propane

Temperature in °K	Pressure in Atm	$H^* - H$, Btu/lb	
		Experimental	Calculated
248.06	2	179.5	178.2
259.33	3	175.2	174.7
268.05	4	171.7	171.8
275.24	5	169.4	169.4
281.44	6	167.1	167.2
286.90	7	165.1	165.2
291.83	8	163.2	163.4
296.30	9	161.4	161.6
300.44	10	159.6	160.0
317.42	15	152.1	152.4
330.70	20	144.5	145.3
341.71	25	137.3	138.3
Average absolute deviation			0.4

Table 5

Enthalpy Departures of Saturated Liquid Nitrogen

Temperature in °K	Pressure in Atm	$H^* - H$, Btu/lb	
		Experimental	Calculated
71.91	0.5	88.1	85.3
74.45	0.7	87.8	84.5
77.35	1	86.5	83.6
83.80	2	83.9	81.6
88.04	3	82.3	80.1
94.09	5	79.7	77.8
98.60	7	77.8	75.8
103.88	10	75.2	73.2
110.57	15	70.5	69.2
115.80	20	65.9	65.2
120.13	25	60.8	60.7
123.86	30	54.8	54.8
Average absolute deviation			1.8

Table 6

Enthalpy Departures of Saturated Liquid Carbon Dioxide

Temperature in °C	Pressure in Atm	$H^* - H$, Btu/lb	
		Experimental	Calculated
-30	14.103	143.2	143.0
-25	16.618	140.7	140.8
-20	19.449	138.3	138.5
-15	22.617	135.4	136.1
-10	26.147	134.2	133.5
-5	30.165	129.3	130.6
0	34.397	126.0	127.6
5	39.172	122.7	124.2
10	44.425	118.6	120.3
15	50.192	113.9	115.9
20	56.525	109.4	110.6
25	63.487	102.7	103.6
Average absolute deviation			1.0

Table 7

Enthalpy Departures of Saturated Liquid Ammonia

Temperature in °K	Pressure in Atm	$H^* - H$, Btu/lb	
		Experimental	Calculated
230	0.5982	600.8	597.0
240	1.0124	590.4	589.1
260	2.526	570.8	573.3
280	5.446	549.4	556.7
300	10.485	528.7	538.9
310	14.063	516.7	529.1
320	18.49	504.2	519.4
330	23.90	491.6	508.8
340	30.42	478.2	497.3
360	47.40	449.8	470.4
380	70.60	417.9	434.9
400	101.5	369.7	375.0
Average absolute deviation			11.0

Table 8

Enthalpy Departures of Methane-Propane Saturated Liquid Mixtures

Mole Fraction Propane	Temperature F	Pressure psia	Experimental	$H^* - H$, Btu/lb			
				Calculated			
				Kay's Rule 1936	Yesavage & Powers 1969	Joffe and Zudkevitch 1970	
0.766 (8)	-144	100	204.5	196.2	197.2	203.2	199.7
	-100	200	193.5	188.2	189.4	194.0	190.7
	-62	300	184.3	181.2	182.5	184.8	181.6
	-24	400	175.6	173.5	175.2	174.4	171.3
	12	500	166.7	165.3	167.4	165.2	161.6
	47	600	158.0	155.4	158.2	154.8	151.6
	76	700	149.5	140.8	145.0	146.5	142.3
	102	800	140.4	132.5	138.0	138.2	134.0
0.052 (9)	-260	10	221.5	217.6	218.0	226.4	222.5
	-200	102	198.6	200.2	200.9	203.5	199.7
	-120	580	157.8	157.0	160.6	170.5	163.0
0.12 (10)	-209	100	210.6	202.9	204.5	211.3	204.7
	-150	300	188.1	183.3	186.0	186.8	180.3
	-124	500	170.9	170.3	174.8	171.8	173.0
	-101	700	159.4	154.7	161.3	161.6	153.3
Average absolute deviation				4.2	2.9	2.7	4.6

Conclusions

For non-polar substances and mixtures, the proposed method gives a quick and fairly accurate estimate of enthalpy departure in the saturated liquid phase up to the critical point.

For polar substances, a better approach is required. This can possibly be done by modifying the temperature function in the second term of the equation.

In general, this empirical equation is simple to use. The coefficients are easily determined from critical properties and experimental enthalpies at the boiling point and the critical point. Even though the procedure is a trial-and-error one, it only takes a few trials to obtain the optimum value of the exponents for each substance.

Nomenclature

a, b, d = coefficients in Benson-Golding and the modified equations

C_1, C_2, \dots, C_9 = constants for evaluating coefficients a, b, d

E_{vap} = heat of vaporization

H^* = ideal gas state enthalpy above datum

H = enthalpy of saturated liquid

m, n = exponents in the modified equation of state

P = pressure

P_c = critical pressure

R = gas constant

T = temperature

T_c = critical temperature

V = volume

v_c = critical volume

z_c = critical compressibility factor

θ = reduced temperature

π = reduced pressure

ϕ = reduced volume

ϕ_b = reduced volume at the boiling point

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A P P E N D I X

Critical Constants of Pure-Components

	P _C Atm	T _C °K	V _C cm ³ /g-mole	Z _C
CH ₄	45.8	191.06	98.72	0.29
C ₃ H ₈	42.1	370.0	200	0.277
N ₂	33.5	126.2	90.094	0.291
CO ₂	72.85	304.2	94.04	0.274
NH ₃	112.5	405.6	72.5	0.242

Source: Reid, R. C. and T. K. Sherwood, "The Properties of Gases and Liquids", 2nd. Ed., 571, 572, 580, 583 (1966)

Pseudocritical Temperatures of Methane-Propane Mixtures

Mole Fraction of Propane in the Mixture	Temperatures in °R	
	Kay's Rule	Yesavage & Powers (Smoothed Optimum Values)
0.766	590.6	601.5
0.052	360.7	364.3
0.12	382.6	391.5

*JUR SUSAN CHITT
 030438 C MFTHANE
 030438 READ,TN
 030444 READ,PK,ZC,AN
 030458 READ,TC,PC,VC,R
 030470 N=1
 030478 1 READ,T,P,V
 030480 TM=1.0-TN
 030498 AP=(1.7/(1.-RK))-ZC
 0304A8 CK=2.25
 0304B6 Q=TC**TM
 0304C0 S=VC**AN
 0304E4 T1=T**TN
 0304FC D=CK*TC-(CK-AP)*Q*T1
 03051A A=R*S*D
 03052A U=VC**1.5
 030540 B=BK*T1
 030540 D2=CK*TC-TM*(CK-AP)*Q*T1
 03056E V=.8*V
 03057A BN=AN+1.0
 030580 4 C=V**(-BN)
 0305A8 E=V**.5
 0305C0 F=V**(-AN)
 0305F0 G=V-B/E
 0305F2 IF(G)6,6,7
 030600 6 V=1.01*(B**0.6667)
 030610 GN TU 4
 030620 7 PI=(R*T/G)-A*C
 03063A PRINT,V,P1
 03064C IF(ABS(P1-P)=0.005)2,2,5
 030674 5 H=V**(-1.5)
 030694 W=V**(-RN-1.0)
 0306P8 W1=R*T*(1.+R**2./2.)/(G**2.)
 0306FA PV=R14*A*W-W1
 0306FE DP=P-P1
 03070A DV=(DP/PV)/2.
 03071A V1=V+DV
 030726 IF(V1-V)2,2,8
 030736 8 V=V1
 03073E GN TU 4
 030742 2 DH=R*T-P1*V+R*S*D2*F/AN
 03075E CH=DH*1.987/82.05
 03077E BH=CH*1.8
 03078A PRINT,DH,CH,BH
 0307A0 PRINT,T,P,V
 0307B4 NN=N+1
 0307C0 IF(N>12)1,1,3
 0307D0 3 STOP
 0307D4 END

*RUN

N.C.E. L&C70 FORTRAN

+.3116796E+02	+.3941366E+04	
+.3165757E+02	+.2529725E+04	
+.3227064E+02	+.1602546E+04	
+.3290444E+02	+.9989721E+03	
+.3379071E+02	+.6107790E+03	
+.3450883E+02	+.3649780E+03	
+.3533796E+02	+.2124101E+03	
+.3594694E+02	+.1201628E+03	
+.3639702E+02	+.6627412E+02	
+.3669047E+02	+.3580257E+02	
+.3684483E+02	+.1947094E+02	
+.3696134E+02	+.1085156E+02	
+.3701239E+02	+.6422607E+01	
+.3703860E+02	+.4177978E+01	
+.3705201E+02	+.3043945E+01	
+.3705674E+02	+.2476562E+01	
+.3706211E+02	+.2191650E+01	
+.3706381E+02	+.2047607E+01	
+.3706455E+02	+.1977050E+01	
+.3706507E+02	+.1941400E+01	
+.3706524E+02	+.1923339E+01	
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+.3706550E+02	+.1905029E+01	
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+.3641545E+02	+.1238266E+03	
+.3593760E+02	+.6903686E+02	
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7	+.5351940E+02	+.2749536E+02
8	+.5352015E+02	+.2749267E+02
9	+.6225167E+05	+.1507544E+04
10	+.1750000E+03	+.2748999E+02
11		+.5352015E+02
12		

END OF JGP

N.C.E. L6070 FORT PAX

*JUN SUSAN CHIEF

030438 C PPUPANE
 030438 KFAD,TN
 030444 RFAD,PK,ZC,AN
 030458 RFAD,TC,PC,VC,R
 030470 N=1
 030478 1 READ,T,P,V
 030480 TM=1.0-TN
 030498 AK=(1. / (1.-RK))=20
 0304AE CK=3.68
 0304B6 Q=TC**TM
 0304CC S=VC**AN
 0304F4 T1=T**TN
 0304FC D=CK*TC-(CK-AK)*Q*T1
 03051A A=R*S*D
 03052A U=VC**1.5
 030540 B=BK*T
 03054C D2=CK*TC-TH*(CK-AK)*Q*T1
 03056E V=.8*V
 03057A BN=AN+1.0
 030586 4 C=V**(-BN)
 0305A8 E=V**,5
 0305C0 F=V**(-AN)
 0305F0 G=V-B/E
 0305F2 IF(G)6,6,7
 030600 6 V=1.01*(B**0.6667)
 03061C GN TU 4
 030620 7 P1=(R*T/G)-A*C
 03063A PPINT,V,P1
 03064C IF(A8*(P1-P)=0.005)2,2,5
 030674 5 H=V**(-1.5)
 030694 W=V**(-BN-1.0)
 030698 W1=R*T*(1.+B**H/2.)/(G**2.)
 0306EA PV=BN*A*W-W1
 0306FE DP=P-P1
 03070A DV=(DP/PV)/2.
 03071A V1=V+DV
 030726 IF(V1-V)2,2,6
 030736 6 V=V1
 03073E GN TU 4
 030742 2 DH=R*T-P1*V+R*S*D2*F/AN
 03076E CH=DH*1.9*7/82.05
 03077E BH=CH*1.8
 03078A PRINT,DH,CH,BH
 0307A0 PRINT,T,P,V
 0307B4 N=N+1
 0307C0 IF(N=12)1,1,3
 0307D0 3 STOP
 0307D4 END

*RJM

N.C.E. L6C70 FORTAN

+.6271998E+02	+.1910503E+04	
+.6414137E+02	+.1199491E+04	
+.6575456E+02	+.7398659E+03	
+.6748021E+02	+.4468857E+03	
+.6909003E+02	+.2633669E+03	
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+.8216053E+02	+.8033935E+01	
+.8216174E+02	+.8016845E+01	
+.8216233E+02	+.8008789E+01	
+.8216264E+02	+.8005126E+01	
+.8216282E+02	+.8002197E+01	
+.1640091E+06	+.3993594E+04	+.7108464E+04
+.2918298E+03	+.8000000E+01	+.8216282E+02
+.7095999E+02	+.4372590E+03	
+.7361134E+02	+.2671926E+03	
+.7616572E+02	+.1613144E+03	
+.7842228E+02	+.9656516E+02	
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+.7731661E+02	+.1450737E+03	
+.7962015E+02	+.8749316E+02	
+.8143493E+02	+.5317578E+02	
+.8277287E+02	+.3333935E+02	
+.8361195E+02	+.2228076E+02	
+.8410400E+02	+.1633129E+02	
+.8437419E+02	+.1321923E+02	
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+.8462651E+02	+.1040942E+02	
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+.9704051E+02	+.2254394E+02	
+.9737207E+02	+.2129296E+02	
+.9754636E+02	+.2065283E+02	
+.9763596E+02	+.2032763E+02	
+.976°136E+02	+.2016406E+02	
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+.9452597E+02	+.6364000E+02	
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+.1007025E+03	+.3744726E+02	
+.1025751E+03	+.3176196E+02	
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+.1051601E+03	+.2594433E+02	
+.1053872E+03	+.2547729E+02	
+.1055045E+03	+.2523950E+02	
+.1055640E+03	+.2512050E+02	
+.1055942E+03	+.2506005E+02	
+.1056092E+03	+.2503002E+02	
+.1056167E+03	+.2501489E+02	
+.1056205E+03	+.2500756E+02	
+.1056224E+03	+.2500415E+02	
+.1056229E+03	+.2500098E+02	

+.3417099E+03

+.2500000E+02

+.1055224E+03

END OF FOR

N.C.E. L6670 FORTRAN

*JLB SUSAN CHTER
 03D438 C NITTRUGEN
 03D438 KREAD,TN
 03D444 KREAD,RK,ZC,AN
 03D458 KREAD,TC,PC,VC,R
 03D470 N=1
 03D478 1 READ,T,P,V
 03D480 TM=1.0-TN
 03D498 AK=(1. / (1. - RK))=ZC
 03D4AE CK=2.34
 03D4B6 Q=TC**TM
 03D4CC S=VC**AN
 03D4E4 TI=TC**TN
 03D4FC D=CK*TC-(RK-AK)*Q*TI
 03D51A A=R*S*D
 03D52A U=VC**1.5
 03D540 B=BK*I'
 03D54C D2=CK*TC-TM*(CK-AK)*Q*TI
 03D56E V=.8*V
 03D57A BN=AN+1.0
 03D586 4 C=V**(-BN)
 03D5A8 E=V**.5
 03D5C0 F=V**(-AN)
 03D5E0 G=V-B/E
 03D5F2 IF(G)6,6,7
 03D600 6 V=1.01*(B**0.6667)
 03D61C GP TO 4
 03D620 7 PI=(R*T/G)-A*P
 03D63A PRINT,V,PI
 03D64C IF(ABS(P1-P)=0.005)2,2,5
 03D674 5 H=V**(-1.5)
 03D694 W=V**(-BN-1.0)
 03D6A8 W1=P*T*(1.+R*B/2.)/(G**2.)
 03D6FA PV=BN*A*W-W1
 03D6FE DP=P+P1
 03D70A DV=(DP/PV)/2.
 03D71A V1=V+DV
 03D726 IF(V1-V)2,2,8
 03D736 8 V=V1
 03D73E GT TO 4
 03D742 2 DH=R*T-P1*V+R*S*D2*F/AN
 03D76E CH=DH*1.987/82.05
 03D77E BH=CH*1.0
 03D78A PRINT,DH,CH,BH
 03D7A0 PRINT,T,P,V
 03D7B4 N=N+1
 03D7C0 IF(N=12)1,1,3
 03D7D0 3 STOP
 03D7F4 END

*RUN

N.C.E. L&C70 FURTAN

+.2759935E+02	+.1315955E+05	
+.2772650E+02	+.8671570E+04	
+.2791145E+02	+.5684378E+04	
+.2816419E+02	+.3690501E+04	
+.2830167E+02	+.2384480E+04	
+.2893256E+02	+.1517573E+04	
+.2945230E+02	+.9504868E+03	
+.3003657E+02	+.5836210E+03	
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+.6436515E+02	+.3000312E+02
+.3521444E+05	+.8527850E+03
+.1238599E+03	+.3000000E+02
	+.1535013E+04
	+.6436518E+02

END OF JOB

*JUB SUSAN CHIEN

030438 C CARPUN DIXIUP
 030438 READ,TN
 030444 READ,PK,ZC,AN
 030458 READ,TC,PC,VC,R
 030470 N=1
 030478 I READ,T,P,V
 030480 TM=1.0-TN
 030498 AK=(1. / (1. -BK)) - ZC
 0304A8 CK=3.58
 0304B6 Q=TC**TM
 0304C0 S=VC**AN
 0304E4 T1=T**TN
 0304F0 D=CK*TC-(CK-AK)*Q*T1
 03051A A=R*S*D
 03052A U=VC**1.5
 030540 B=BK*I'
 03054C D2=CK*TC-TM*(CK-AK)*Q*T1
 03056E V=.8*V
 03057A BN=AN+1.0
 030586 4 C=V**(-BN)
 0305A8 E=V**.5
 0305C0 F=V**(-AN)
 0305F0 G=V+b/E
 0305F2 IF(G)6,6,7
 030600 6 V=1.01*(B**0.6667)
 03061C GO TU 4
 030620 7 P1=(R*T/G)-A*F
 03063A PRINT,V,P1
 03064C IF(ABS(P1-F)=0.005)2,2,5
 030674 5 H=V**(-1.5)
 030694 W=V**(-BN-1.0)
 0306B8 W1=R*T*(1.+R*T/2.)/(G**2.)
 0306FA PV=BN*A*W-W1
 0306FE DP=P-P1
 03070A DV=(DP/PV)/2.
 03071A V1=V+DV
 030726 IF(V1-V)2,2,6
 030736 8 V=V1
 03073E GO TU 4
 030742 2 DH=R*T-P1*V+K*S*D?*F/AN
 03076E CH=DH*1.9E7/82.05
 03077E BH=CH*1.8
 03078A PRINT,DH,CH,BH
 0307A0 PRINT,T,P,V
 0307B4 N=N+1
 0307C0 IF(N=12)1,1,3
 0307D0 3 STOP
 0307D4 END

*RUN

N.C.E. LEC70 FORTAN

+.3276794E+02	+.8517805E+03	
+.3395991E+02	+.5198417E+03	
+.3511464E+02	+.3120154E+03	
+.3613920E+02	+.1860063E+03	
+.3696183E+02	+.1101516E+03	
+.3755407E+02	+.6615195E+02	
+.3793713E+02	+.4154199E+02	
+.3816311E+02	+.2826293E+02	
+.3828765E+02	+.2131152E+02	
+.3935339E+02	+.1773950E+02	
+.3939719E+02	+.1593164E+02	
+.3940434E+02	+.1502026E+02	
+.3941297E+02	+.1456170E+02	
+.3941731E+02	+.1433270E+02	
+.3941947E+02	+.1421997E+02	
+.3942057E+02	+.1416162E+02	
+.3942112E+02	+.1413232E+02	
+.3942140E+02	+.1411791E+02	
+.3942153E+02	+.1411083E+02	
+.3942160E+02	+.1410693E+02	
+.1443673E+06	+.3496133E+04	+.6293035E+04
+.2431599E+03	+.1410299E+02	+.3842160E+02
+.3343998E+02	+.7145598E+03	
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+.3591790E+02	+.2636567E+03	
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+.6359220E+02	+.6350659E+02	
+.6367203E+02	+.6349633E+02	
+.6360660E+02	+.6349218E+02	
+.6360920E+02	+.6349925E+02	
+.1045412E+06	+.2531658E+04	+.4557000E+04
+.2981595E+03	+.6348699E+02	+.6360920E+02

END OF JUR

N.C.F. L6C70 FURTAN

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038408 C AMMONIA
038408 READ,TH
038414 READ,PK,ZC,AN
038428 READ,TC,PC,VC,R
038440 N=1
038448 I READ,T,P,V
038450 IM=1.0+TN
038468 AK=(1. / (1.+BK))-ZC
03847E CK=3.49
038486 Q=TC**TM
038490 S=VC**AN
038494 T1=T**TN
038496 U=CK*TC-(CK-AK)*Q*T1
0384FA A=R*S*D
0384FA U=VC**1.5
038A10 B=BK*U
038A1C U2=CK*TC-TM*(CK-AK)*Q*T1
038A2E V=.8*V
038A4A BN=AN+1.0
038A56 4 C=V**(-BN)
038A78 E=V**,5
038A90 F=V**(-AN)
038AP0 G=V-B/E
038AC2 IF(G)6,6,7
038AD0 6 V=1.01*(D**0.6667)
038AFC UN TU 4
038AF0 7 P1=(R*T/G)-A*C
038B0A PRINT,V,P1
038B1C IF(ABS(P1-P)=0.005)2,2,5
038B44 5 H=V**(-1.5)
038B64 W=V**(-BN-1.0)
038B88 W1=R*T*(1.+R**1/2.)/(G**2.)
038B9A PV=RN*A*W-W1
038BCE DP=P-P1
038BD4 DV=(DP/PV)/2.
038BFA V1=V+DV
038BF6 IF(V1-V)<2.0
038CC6 8 V=V1
038CDE UN TU 4
038C12 2 DH=R*T-P1*V+R*S*D2*F/AN
038C3E CH=DH*1.977/02.05
038C4E BH=CH*1.0
038C5A PRINT,DH,CH,BH
038C70 PRINT,T,P,V
038C94 N=N+1
038C90 IF(N=12)1,1,3
038CA0 3 STOP
038CA4 END

```

*RUM

N.C.F. 16070 FURTAN

+.1963990E+02	+.1542976E+02	
+.1960110E+02	+.9928941E+04	
+.2020864E+02	+.6290320E+04	
+.2050630E+02	+.3928060E+04	
+.2100320E+02	+.2397595E+04	
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+.2662353E+02	+.1409796E+02	
+.2662364E+02	+.1409001E+02	
+.2662366E+02	+.1407348E+02	
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+.3100000VF+03	+.1406299E+02	+.2602373E+02
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+.2564980E+02	+.3375332E+03	
+.2629846E+02	+.1972573E+03	
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+.2705610E+02	+.6980737E+02	
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	+.3759377E+02	+.7060473E+02	
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	+.4378683E+02	+.1200622E+03	
	+.4554724E+02	+.1142214E+03	
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	+.4800152E+02	+.1048554E+03	
	+.4884104E+02	+.1032076E+03	
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	10.00000E+02	10.00000E+03	

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3	+.4991350E+02	+.1015314E+03	
4	+.4991415E+02	+.1015161E+03	
5	+.4991958E+02	+.1015078E+03	
6	+.4992222E+02	+.1015046E+03	
7	+.1402601E+06	+.3541971E+04	+.6375542E+04
8	+.4000000E+03	+.1015000E+03	+.4992222E+02
9			
10			
11			
12			

END OF JOB

N.C.E. L6070 FURTRAN

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347.4 28.0 112.0
03A108 C RAY
03A108 C METHANE
03A108 READ,TN
03A114 READ,PK,2C,AN
03A128 READ,TC,PC,VC,R
03A140 N=1
03A148 1 READ,T,P,V
03A150 TM=1.0-TN
03A168 AK=(1.0/(1.0-PK))-2C
03A17E CK=2.25
03A186 Q=1C**TM
03A190 S=VC**AN
03A1P4 T1=T**TN
03A1CC U=CK*TC-(CK-AK)*Q*T1
03A1FA A=R*S*D
03A1FA U=VC**1.5
03A210 B=BK*11
03A21C D=CK*TC-TM*(CK-AK)*Q*T1
03A23E V=,R*V
03A24A BN=AN+1.0
03A256 4 C=V**(-BN)
03A278 E=V**.5
03A290 F=V**(-AN)
03A2B0 G=V-B/E
03A2C2 IF(G)6,6,7
03A2D0 6 V=1.01*(-6**0.6667)
03A2FC GN TU 4
03A2F0 7 P1=(R*T/G)-A*C
03A30A PRINT,V,P1
03A31C IF(ABS(P1-P)=0.005)2,2,5
03A344 5 H=V**(-1.5)
03A364 W=V**(-BN-1.0)
03A3P8 W1=R*T*(1.0+R*B/2.0)/(G**2.0)
03A3PA PV=BH*A*W-W1
03A3CE DP=P-P1
03A3PA DV=(DP/PV)/2.
03A3FA V1=V+DV
03A3F6 IF(V1-V)2,2,6
03A406 8 V=V1
03A40E GN TU 4
03A412 2 DH=R*T-P1*V+R*S*D2*F/AN
03A43E CH=DH*1.497/82.05
03A44E BH=CH*1.0
03A45A PRINT,DH,CH,BH
03A470 PRINT,T,P,V
03A484 N=N+1
03A490 IF(N=15)1,1,2
03A4A0 3 STOP
03A4A4 END

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*RUN

M.C.E. L6670 FORTRAN

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+.3034626E+02	+.1111823E+02
+.3054436E+02	+.7277710E+04
+.3081617E+02	+.4726574E+04
+.3117561E+02	+.3037702E+04
+.3162852E+02	+.1925592E+04
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+.5734739E+02	+.3191040E+02	
+.5962800E+03	+.1444009E+04	+.2599215E+04
+.1793999E+03	+.3190699E+02	+.5734739E+02

END OF IUP

N.C.E. 18070 FURTRAN

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XT(I)=XT(I)+X(I)
03A108 C KAY
03A108 C PROPANE
03A108 KFAD,TN
03A114 KFAD,PK,LC,AN
03A128 KFAD,TG,PC,VC,R
03A140 N=1
03A148 1 KFAD,T,P,V
03A150 TM=1.0-TN
03A168 AK=(1. / (1.-RK))=20
03A17E CK=3.68
03A186 Q=TC**TM
03A190 S=VC**AN
03A1P4 T1=T**TN
03A1CC D=CK*TC-(CK-AK)*Q*T1
03A1EA A=R*S*D
03A1FA U=VC**1.5
03A210 B=BK*II
03A21C D2=CK*TC-TM*(CK-AK)*Q*T1
03A22E V=.8*V
03A24A BN=AN+1,0
03A250 4 C=V**(-BN)
03A278 E=V**,5
03A290 F=V**(-AN)
03A2R0 G=V-U/E
03A2C2 IF(G)6,6,7
03A2D0 6 V=1.01*(B**0.6667)
03A2EC GN TU 4
03A2F0 7 P1=(R*T/G)-A*C
03A30A PRINT,V,P1
03A31C IF(A8S(P1-F)=0.005)2,2,5
03A344 5 H=V**(-1.5)
03A364 W=V**(-BN-1,0)
03A388 W1=R*T*(1.+B**H/2.)/(G**2.)
03A3FA PV=BN*A**W-W1
03A3CE DP=P-P1
03A3DA DV=(DP/PV)/2.
03A3FA V1=V+DV
03A3F6 IF(V1-V)2,2,8
03A400 8 V=V1
03A40E GN TU 4
03A412 2 DH=R*T-P1*V+R*S*U2*F/AN
03A43E CH=DH*1.9*7/82.05
03A44E BH=CH*1.0
03A45A PRINT,DH,CH,BH
03A470 PRINT,T,P,V
03A484 N=N+1
03A490 IF(N=15)1,1,3
03A4A0 3 STOP
03A4A4 END

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*RUN

N.C.E. L6070 FURTRAN

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+.5910750E+02	+.1092770E+03
+.5958123E+02	+.7143242E+04
+.6010423E+02	+.4630074E+04
+.6078952E+02	+.2967225E+04
+.6164204E+02	+.1873501E+04
+.6262471E+02	+.1160729E+04
+.6370005E+02	+.7024152E+03
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+.6633264E+02	+.1295986E+03
+.6680522E+02	+.6910653E+02
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	+.1109950E+03	+.2800659E+02
	+.1109980E+03	+.2800268E+02
	+.1353053E+06	+.3276681E+04
	+.3473999E+03	+.2800000E+02
		+.1109980E+03

END UF JOB

N.C.E. L6670 FORTRAN

```

175.2 27.69 53.
03A108 C YESAVAGE
03A108 C METHANE
03A108 READ,TN
03A114 READ,RK,ZC,AN
03A128 READ,TC,PC,VC,K
03A140 N=1
03A148 1 READ,T,D,V
03A150 TM=1.0-TN
03A168 AK=(1. / (1. - RK)) - ZC
03A17E CK=2.25
03A186 Q=TC**TM
03A19C S=VC**AN
03A1P4 TI=TC**TN
03A1CC D=CK*TC-(CK-AK)*Q*TI
03A1FA A=R*S*D
03A1FA U=VC**1.5
03A210 B=BK*U
03A21C D2=CK*TC-TM*(CK-AK)*Q*TI
03A23E V=.8*V
03A24A BN=AN+1.0
03A256 4 C=V**(-BN)
03A278 E=V**.5
03A290 F=V**(-AN)
03A2D0 G=V-B/E
03A2C2 IF(C)6,6,7
03A2D0 6 V=1.01*(B**0.5667)
03A2FC GN TU 4
03A2F0 7 P1=(R*T/G)-A*C
03A3CA PRINT,V,P1
03A31C IF(ABS(P1-F)=0.005)2,2,5
03A344 5 H=V**(-1.5)
03A364 W=V**(-BN-1.0)
03A388 W1=P*T*(1.+R**1/2.1/(G**2.))
03A39A PV=BN*A*W-W1
03A3CE UP=P-P1
03A3DA DV=(UP/PV)/2.
03A3FA V1=V+DV
03A3F6 1F(V1-V)Z,Z,0
03A406 d V=V1
03A40E GN TU 4
03A412 2 DH=R*T-P1*V+K*S*D*F/AN
03A43E CH=DH*1.997/02.05
03A44E BH=CH*1.8
03A45A PRINT,DH,CH,BH
03A470 PRINT,T,K,V
03A484 N=N+1
03A490 1F(N=15)1,1,3
03A4A0 3 STOP
03A4A4 END

```

*RUN

N.C.F. L6070 FURTPAN

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+.3034603E+02	+.1092770E+05	
+.3054353E+02	+.7150046E+04	
+.3081390E+02	+.4640970E+04	
+.3117065E+02	+.2960209E+04	
+.3161646E+02	+.1887062E+04	
+.3214651E+02	+.1173756E+04	
+.3272279E+02	+.7140810E+03	
+.3320604E+02	+.4229753E+03	
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+.3478010E+02	+.1976023E+02	
+.3483572E+02	+.1019580E+02	
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+.3488700E+02	+.1603515E+01	
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END OF JDR

N.C.E. LAG70 FORTRAN

```

339.28 23.896 105.
03A108 C YESAVAGE
03A108 C PROPANE
03A108 READ,TN
03A114 READ,BK,ZC,AN
03A128 READ,TC,PC,VU,R
03A140 N=1
03A148 1 READ,T,P,V
03A150 TM=1.0-TN
03A168 AK=(1./(1.-BK))-ZC
03A17E CK=3.68
03A186 Q=TC**TM
03A190 S=VC**AN
03A194 T1=T**TN
03A1CC D=CK*TC-(CK-AK)*Q*T1
03A1EA A=R*S*D
03A1FA U=VC**1.5
03A210 B=BK*U
03A21C D2=CK*TC-TM*(CK-AK)*Q*T1
03A23E V=.8*V
03A24A BN=AN+1.0
03A256 4 C=V**(-BN)
03A278 E=V**.5
03A290 F=V**(-AN)
03A2P0 G=V-B/E
03A2C2 IF(G)6,6,7
03A2D0 6 V=1.01*(B**0.4667)
03A2FC GN TU 4
03A2F0 7 P1=(K*T/G)-A*C
03A30A PRINT,V,P1
03A31C IF(ABS(P1-P)=0.005)2,2,5
03A344 5 H=V**(-1.5)
03A364 W=V**(-BN-1.0)
03A388 W1=R*T*(1.+B**4/2.)/(G**2.)
03A39A PV=BN*A*W-W1
03A3CE DP=P-P1
03A3DA DV=(DP/PV)/2.
03A3EA V1=V+DV
03A3F6 IF(V1-V)2,2,6
03A406 8 V=V1
03A40E GN TU 4
03A412 2 DH=R*T-P1*V+K*S*D*F/AN
03A43E CH=DH*1.987/82.05
03A44E BH=CH*1.8
03A45A PRINT,DH,CH,BH
03A470 PRINT,T,P,V
03A484 N=N+1
03A490 IF(N=15)1,1,3
03A4A0 3 STOP
03A4A4 END

```

*RUN

N.C.E. L6670 FURTPAN

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+.5919683E+02	+.1069907E+05
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END OF JOB