Liquid Phase Enthalpy Values for the Methane-Ethane System

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IN PREVIOUS investigations (*8, 10, 11*) saturated liquid phase enthalpies have been calculated for five binary hydrocarbon systems over the pressure range 100 to 600 p.s.i.a. These enthalpy data were calculated from P-V-T-x data and the differential heat of condensation. The basic relationships, which are thermodynamically rigorous, employed are given by Dodge (*7*) and are

$$\left(\frac{\partial P}{\partial T}\right)_y = \frac{\Delta H_c}{T\Delta V_c} \tag{1}$$

$$\Delta V_c = V_b - V_d + (y - x)\left(\frac{\partial V_G}{\partial y}\right)_{T,\,P} \tag{2}$$

$$\Delta H_c = H_b - H_d + (y - x)\left(\frac{\partial H_G}{\partial y}\right)_{T,\,P} \tag{3}$$

The Benedict-Webb-Rubin (*3, 4*) equation of state

$$P = RT\mathrm{d} + (B_oRT\text{-}A_o\text{-}C_o/T^2)\mathrm{d}^2 + (b'RT2a')\mathrm{d}^3 + a'\alpha\mathrm{d}^6 + c\mathrm{d}^3/T^2[(1 + \gamma\mathrm{d}^2)\exp(-\gamma\mathrm{d}^2)] \tag{4}$$

was checked against the available vapor phase volume for the various hydrocarbon systems and found useful. Usually the difference between the experimental and the predicted values was less than ±1%. The Benedict-Webb-Rubin equation was then used to calculate additional volumetric data and the necessary partial volumes were obtained by graphical differentiation.

The form of the Benedict-Webb-Rubin equation

$$H - \sum_i x_iH_i^\circ = (B_oRT - 2A_o - 4C_o/T^2)\mathrm{d} + (2b'RT - 3a')\mathrm{d}\,{}^{3}\!/_{2} + 6a'\alpha\mathrm{d}\,{}^{5}\!/_{5} + c\mathrm{d}^2/T^2 \left[3\,\frac{1 - \exp(-\gamma\mathrm{d}^2)}{{}^{2}\mathrm{d}^2} - \frac{\exp(-\gamma\mathrm{d}^2)}{2} + \exp(\gamma\mathrm{d}^2)\right] \tag{5}$$

in conjunction with ideal gas state enthalpies obtained from API Research Project 44 (*1*) were used to predict total enthalpy values for gas mixtures. Partial enthalpy values were then obtained by graphical differentiation. With the calculated enthalpy and volumetric data and experimental vapor-liquid equilibrium data, and information on the volumetric behavior of the saturated liquid phase, the differential heat of vaporization and, in turn, saturated liquid phase enthalpies could be calculated by Equations 1, 2, and 3.

While liquid phase enthalpy data of saturated mixtures are useful and of interest, partial values—in a sense—are more useful because the contribution of each component to the total enthalpy of the mixture is known. With this thought in mind this work was undertaken to evaluate partial enthalpies in the liquid phase for the methane-ethane system. This binary system was selected because it is of some industrial interest and extensive P-V-T-x data have been determined by Bloomer, Gami, and Parent (*6*).

One method of obtaining partial enthalpy values is to calculate saturated enthalpies by Equations 1, 2, and 3 at a number of different pressures and, if the effect of pressure on the liquid phase enthalpy is negligible, which is certainly a valid assumption if the pressure range is small, then draw in various isotherms on a plot of enthalpy *vs.* composition. From the slope of an isotherm at a given point, the partial enthalpy values of the components of the particular mixture at the specific conditions of temperature and pressure can be evaluated.

An attempt was made to determine partial enthalpies by this procedure. Saturated liquid enthalpies were calculated at intervals of 50 p.s.i. over the pressure range of 100 to 700 p.s.i.a. The results were not consistent and clearly partial enthalpies could not be estimated. While the method employed is thermodynamically rigorous, certain difficulties arise when attempts are made to evaluate some of the required terms.

Since the results obtained using the differential heat of condensation were unsatisfactory, it was decided to work with the differential heat of vaporization. A similar type of reasoning used to develop Equations 1, 2, and 3 for a condensation process can be applied to a vaporization process and an analogous set of equations developed. The equations in the latter case would be

$$\left(\frac{\partial P}{\partial T}\right)_x = \frac{\Delta H_v}{T\Delta V_v} \tag{6}$$

$$\Delta V_v = V_d - V_b - (y - x)\left(\frac{\partial V_L}{\partial x}\right)_{T,\,P} \tag{7}$$

$$\Delta H_v = H_d - H_b - (y - x)\left(\frac{\partial H_L}{\partial x}\right)_{T,\,P} \tag{8}$$

ΔH_v represents the differential heat of vaporization, which is the heat required to vaporize a mole of mixture of composition y_1 from a large quantity of liquid of composition x_1. The composition of the liquid remains unchanged in the process and the relationship between y_1 and x_1 is the equilibrium condition. With the experimental data available, the effect of pressure on the liquid volume over a 50-p.s.i. pressure differential had to be neglected. This effect is undoubtedly negligible. In other words, in evaluating ΔV_v by Equation 7, $(\partial V_L/\partial x)_T$ was used in place of $(\partial V_L/\partial x)_{T,\,P}$. With this value and the experimental data, the differential heat of vaporization could be determined from Equation 6.

If the original value of the liquid phase enthalpy as calculated by Equations 1, 2, and 3 had been correct, the term $(\partial H_L/\partial x)_{T,\,P}$ could have been calculated directly from Equation 8 and no further work would have been necessary. At pressures of 450 and 500 p.s.i.a. this type of straightforward solution was obtained. To show how well the procedure worked in these instances, plots of ΔH_c *vs.* x and ΔH_v *vs.* x at 500 p.s.i.a. are included as Figures 1 and 2, respectively. The differential heats calculated by Equations 1 and 6 are compared graphically with those obtained from Equations 3 and 8, in which the final results were substituted.

This was not the situation in the majority of the cases, however, and adjustments had to be made in the values of the saturated liquid phase enthalpies, H_b's. Any alteration in the value of H_b meant a change of the same magnitude in $(y - x)(\partial H_L/\partial x)_T$, specifically the second term of the product, because Equation 6 must be satisfied. Naturally, in doing this Equation 3 was no longer satisfied. A trial and error procedure was then employed to obtain a set of values of H_b's and $(y - x)$ $(\partial H_L/\partial x)_T$ which was consistent with Equations 6, 7, and 8.

Basically, the assumption was made that the differential heat of vaporization was more accurate than the differential heat of condensation. The reasons for assuming this were: (1) $(\partial P/\partial T)_x$ showed less variation than $(\partial P/\partial T)_y$. The variations in the latter quantity were particularly large at high methane concentrations. (2) Partial volumes and partial enthalpies in the gas phase were obtained from an equation of state; consequently, these values are subject to error. Contrariwise, the partial volumes in the liquid phase could be obtained from the available experimental data, provided the effect of an additional pressure of 50 p.s.i. was neglected. (3) Partial enthalpies in the liquid phase were, in essence, the final answer and were not used in the calculation. This was not true of partial enthalpies in the gas phase. These gas phase partial enthalpies may well be a source of error. (4) ΔV_v was frequently approximately the magnitude of V_d. This was not true of the relationship between ΔV_c and V_d, since partial gas phase volumes were much larger than partial liquid phase volumes. Dew point volumes are accurate, as these values were obtained by the Benedict equation of state which was checked against experimental values and modified by Bloomer and others (*6*) to obtain good agreement in this area. One would conclude that ΔV_v tended to be more accurate than ΔV_c.

Usually the differential heat of condensation appeared to be too large by from 200 to 400 B.t.u.'s per pound mole. Only in a few instances did the differential heat of condensation appear to be too small. A plot of ΔH_c *vs.* x at a pressure of 650 p.s.i.a is included as Figure 3 to show the deviation between the calculated values and the values finally used. The maximum difference in this particular instance was 400 B.t.u. per lb. mole; hence, the illustration reflects the maximum deviation. For comparison a plot (Figure 4) of ΔH_v *vs.* x at 650 p.s.i.a is also included. Here the differences between the calculated and final values are small.

Only at pressures of 100 and 150 p.s.i.a. did the ΔH_c values appear to be more accurate than the ΔH_v's. Here the properties of the gaseous mixture tended to be the direct combination of the properties of the pure components.

As a further check on the gas phase volumes and partial volumes used in the calculations, these values at 70 mole % methane were determined using the relationship presented by Black (*5*).

$$V_m = \frac{RT}{P} + \sum b_i y_i - \frac{[\sum (a_i \zeta^*_i)^{0.5} y_i]^2}{RT} \tag{9}$$

The volumes calculated by Equation 9 were in good agreement with the experimental values and those determined by the Benedict-Webb-Rubin equation. However, the partial volumes determined by the relationship

$$V_i = \frac{RT}{P} + b_i - \frac{a_i \zeta_i}{RT} + \frac{(\sum_{j=1}^{n} G_{ij} y_j)^2}{RT} \tag{10}$$

also given by Black, differed by ±12% from those obtained by the Benedict-Webb-Rubin equation. This points out the difficulties involved in calculating partial volumes from an equation of state. The equation may predict the total volume reasonably well, but be in error in the partial volume. To determine whether the partial volumes predicted by one equation of state are more accurate than those predicted by another equation would be rather difficult.

The final liquid phase enthalpy data are illustrated on Figure 5 and Table I. The enthalpies presented differ from those given previously (*10*). The former values were obtained by use of the differential heat of condensation, while the values presented here are based chiefly on the differential heat of vaporization. For the reasons mentioned, the new values are believed to be the more accurate.

Also given in Table I are bubble point and dew point temperatures, dew point enthalpies, and partial enthalpies for the liquid phase. The pure component data are those of Matthews and Hurd (*9*) for methane and of Barkelew, Valentine, and Hurd (*2*) for ethane. The partial enthalpies and ethane are shown in Figures 6 and 7, respectively. For comparison the saturation curves for the pure substances are comparison the saturation curves for the pure substances are included on each figure. While quantitative conclusions cannot be reached, composition, temperature, and pressure are clearly important parameters in the evaluation of partial enthalpy values.

"Ideal" enthalpy values, assuming additive properties and estimating the effect of pressure on the enthalpy of the pure components, of the saturated liquid were calculated for pressures of 100 and 200 p.s.i.a. over the composition ranges for which the bubble point temperature of the mixture did not exceed the critical temperature of methane. In Figure 8, these values are compared with the enthalpies of the real mixture calculated in this work. The comparisons indicate the integral heat of solution per mole of mixture is relatively small. This is to be expected in a mixture of paraffin hydrocarbons at conditions which are not severe.

ACKNOWLEDGMENT

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NOMENCLATURE

H = enthalpy, B.t.u. per lb. mole
ΔH_c = differential heat of condensation, B.t.u. per lb. mole

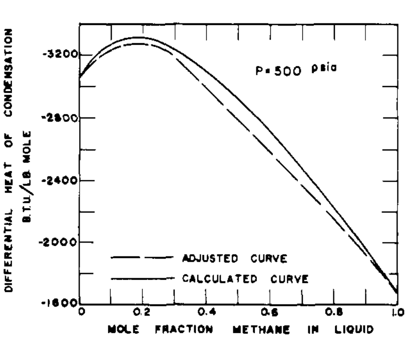

Figure 1. Calculated and adjusted ΔH_c values

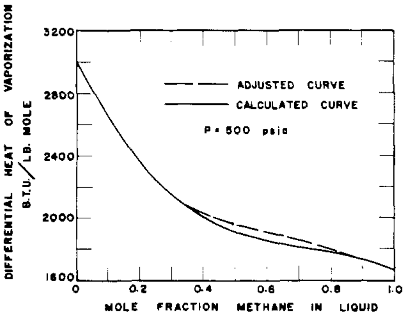

Figure 2. Calculated and adjusted ΔH_v values

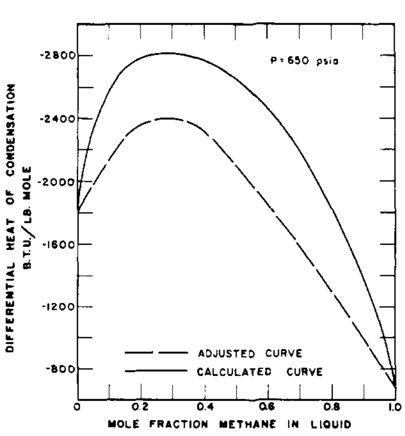

Figure 3. Calculated and adjusted ΔH_c values

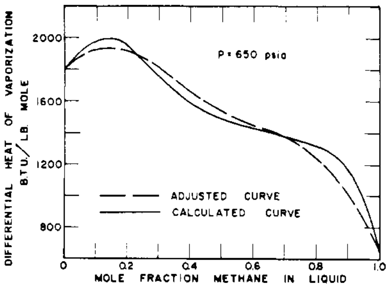

Figure 4. Calculated and adjusted ΔH_v values

Table I. Enthalpy and Partial Enthalpy Values for Saturated Mixtures of Methane and Ethane[a]

Mole Fraction Methane	Temp., ° F.		Enthalpy, B.t.u./Lb. Mole			
	t_b	t_d	H_b	H_d	$\bar{H}_1$	$\bar{H}_2$
	Pressure = 100 p.s.i.a.					
0	−46.0	−46.0	−2060	3299		−2061(*2*)
0.10	−101.7	−52.2	−2765	3242	+118	−3085
0.20	−136.3	−58.5	−3048	3182	−495	−3686
0.30	−156.0	−65.0	−3074	3112	−743	−4073
0.40	−171.2	−72.7	−2982	3031	−887	−4379
0.50	−181.1	−80.9	−2795	2933	−988	−4602
0.60	−187.5	−90.7	−2537	2848	−1065	−4745
0.70	−192.8	−102.2	−2235	2735	−1125	−4825
0.80	−197.3	−117.7	−1914	2598	−1173	−4878
0.90	−201.6	−140.0	−1581	2396	−1210	−4920
1.00	−205.5	−205.5	−1244	1812	−1244	(*9*)

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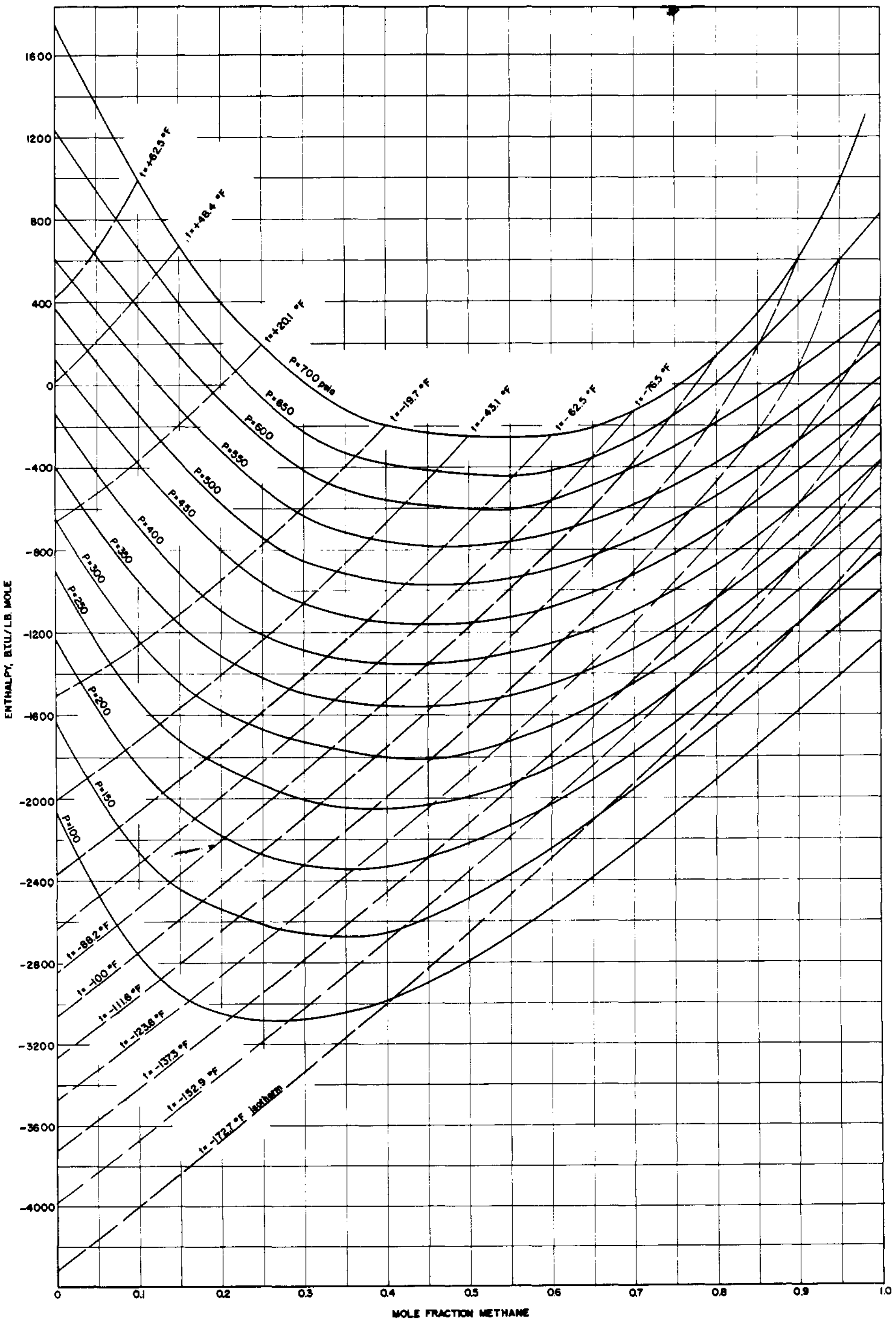

Figure 5. Enthalpy-composition diagram

H = 0 for pure components in ideal gas state, unit fugacity, and 0° R.

Table I. (*Continued*)

Mole Fraction Methane	Temp., ° F.		Enthalpy, B.t.u./Lb. Mole			
	t_b	t_d	H_b	H_d	$\bar{H}_1$	$\bar{H}_2$
Pressure = 150 p.s.i.a.						
0	−24.2	−24.2	−1630	3400		−1630(*2*)
0.10	−74.0	−30.2	−2279	3339	570	−2596
0.20	−106.6	−37.4	−2540	3274	+22	−3181
0.30	−131.1	−44.9	−2658	3202	−418	−3618
0.40	−149.5	−53.5	−2654	3121	−637	−3999
0.50	−161.0	−62.2	−2487	3028	−760	−4214
0.60	−169.0	−73.2	−2246	2920	−821	−4384
0.70	−175.4	−87.0	−1958	2795	−900	−4427
0.80	−180.6	−103.0	−1650	2646	−947	−4462
0.90	−185.6	−127.7	−1330	2428	−979	−4489
1.00	−190.0	−190.0	−1002	1852	−1002	(*9*)
Pressure = 200 p.s.i.a.						
0	−6.2	−6.2	−1231	3467		−1231(*2*)
0.10	−51.0	−13.4	−1850	3413	850	−2150
0.20	−85.5	−20.9	−2181	3344	+455	−2840
0.30	−112.0	−29.0	−2323	3263	−90	−3280
0.40	−130.0	−37.9	−2327	3170	−388	−3620
0.50	−144.0	−48.5	−2222	3069	−534	−3910
0.60	−154.0	−60.9	−2015	2952	−578	−4170
0.70	−161.2	−75.0	−1785	2820	−656	−4420
0.80	−167.1	−92.2	−1490	2661	−700	−4650
0.90	−172.7	−117.7	−1163	2423	−750	−4876
1.00	−178.5	−178.5	−811	1866	−811	(*9*)
Pressure = 250 p.s.i.a.						
0	+8.8	+8.8	−901	3545		−901(*2*)
0.10	−34.0	+1.9	−1530	3468	1400	−1855
0.20	−68.3	−7.4	−1841	3387	715	−2480
0.30	−95.4	−16.2	−2004	3301	+308	−2995
0.40	−115.3	−25.9	−2050	3207	−93	−3355
0.50	−130.0	−37.1	−1992	3102	−334	−3650
0.60	−141.4	−50.5	−1852	2984	−473	−3920
0.70	−149.0	−65.1	−1617	2845	−531	−4150
0.80	−155.6	−83.6	−1323	2676	−561	−4370
0.90	−162.1	−109.8	−999	2451	−601	−4580
1.00	−168.2	−168.2	−652	1868	−652	(*9*)
Pressure = 300 p.s.i.a.						
0	+21.6	21.6	−650	3515		−650(*2*)
0.10	−18.2	13.1	−1238	3459	1319	−1522
0.20	−52.6	+4.2	−1578	3398	1040	−2233
0.30	−80.2	−5.2	−1728	3321	650	−2747
0.40	−102.4	−15.7	−1802	3327	+246	−3167
0.50	−118.0	−27.5	−1782	3118	−62	−3502
0.60	−129.9	−41.2	−1652	2994	−240	−3770
0.70	−138.6	−56.9	−1450	2850	−345	−4028
0.80	−145.9	−96.3	−1180	2681	−415	−4240
0.90	−152.9	−103.8	−859	2432	−467	−4387
1.00	−159.2	−159.2	−502	1853	−502	(*9*)
Pressure = 350 p.s.i.a.						
0	+32.9	32.9	−400	3511		−400(*2*)
0.10	−5.6	23.5	−971	3453	1860	−1286
0.20	−38.1	14.0	−1298	3372	1350	−1960
0.30	−67.2	+4.2	−1500	3318	893	−2526
0.40	−90.0	−7.0	−1558	3221	496	−2927
0.50	−107.0	−19.2	−1542	3113	+185	−3269
0.60	−119.8	−33.3	−1453	2990	0	−3633
0.70	−129.0	−49.9	−1282	2844	−125	−3982
0.80	−135.2	−70.4	−1041	2658	−225	−4305
0.90	−144.6	−98.1	−728	2408	−305	−4535
1.00	−151.8	−151.8	−370	1830	−370	(*9*)
Pressure = 400 p.s.i.a.						
0	43.0	43.0	−135	3495		−135(*2*)
0.10	+6.6	33.2	−687	3456	2167	−1004
0.20	−27.0	23.4	−1092	3389	1625	−1771
0.30	−55.0	12.6	−1288	3305	1141	−2329
0.40	−79.2	+0.4	−1353	3203	738	−2747
0.50	−96.7	−11.8	−1337	3092	420	−3094
0.60	−109.7	−26.8	−1253	2960	250	−3508
0.70	−120.0	−44.1	−1100	2818	+100	−3900
0.80	−129.1	−64.8	−877	2639	−27	−4277
0.90	−137.2	−93.7	−574	2392	−138	−4498
1.00	−145.2	−145.2	−237	1803	−237	(*9*)
Pressure = 450 p.s.i.a.						
0	52.3	52.3	+119	3458		+119(*2*)
0.10	+18.0	41.5	−380	3410	2575	−708
0.20	−13.3	30.9	−800	3358	2000	−1500
0.30	−43.1	20.1	−1060	3290	1464	−2142
0.40	−67.5	+7.7	−1152	3205	1020	−2600
0.50	−87.0	−5.7	−1159	3081	655	−2973
0.60	−140.0	−21.7	−1081	2953	433	−3352
0.70	−112.5	−39.0	−922	2800	298	−3769
0.80	−121.1	−60.6	−701	2615	185	−4245
0.90	−130.0	−90.0	−419	2331	+60	−4730
1.00	−138.8	−138.8	−98	1763	−98	(*9*)
Pressure = 500 p.s.i.a.						
0	61.0	61.0	+364	3398		+364(*2*)
0.10	+28.0	49.4	−141	3350	3270	−520
0.20	−3.8	38.3	−573	3302	2335	−1300
0.30	−32.2	26.9	−856	3249	1767	−1980
0.40	−57.3	+13.9	−957	3163	1373	−2510
0.50	−77.1	0.0	−966	3050	908	−2840
0.60	−92.4	−16.4	−893	2916	622	−3165
0.70	−104.6	−34.3	−749	2768	475	−3605
0.80	−114.1	−56.4	−540	2587	375	−4200
0.90	−123.5	−86.6	−273	2291	241	−4897
1.00	−133.1	−133.1	+30	1715	30	(*9*)
Pressure = 550 p.s.i.a.						
0	68.9	68.9	605	3307		+605(*2*)
0.10	37.2	56.4	+118	3282	3700	−280
0.20	+6.8	44.8	−312	3253	2740	−1075
0.30	−22.0	32.9	−638	3212	2027	−1780
0.40	−47.5	19.7	−760	3140	1640	−2360
0.50	−68.3	+5.2	−784	3016	1142	−2710
0.60	−83.8	−11.9	−720	2882	870	−3105
0.70	−96.7	−30.2	−580	2727	727	−3630
0.80	−107.4	−52.4	−378	2541	570	−4170
0.90	−117.4	−82.9	−112	2238	420	−4900
1.00	−127.5	−127.5	+195	1655	195	(*9*)
Pressure = 600 p.s.i.a.						
0	75.8	75.8	870	3195		+870(*2*)
0.10	46.5	62.9	+380	3191	4260	−51
0.20	+16.6	50.7	−70	3172	3030	−845
0.30	−12.2	38.2	−413	3127	2380	−1610
0.40	−37.0	24.6	−550	3045	1860	−2157
0.50	−59.5	+9.9	−605	2931	1415	−2625
0.60	−77.0	−7.6	−561	2801	1120	−3083
0.70	−90.0	−26.7	−401	2656	1000	−3670
0.80	−101.0	−49.6	−183	2466	980	−4835
0.90	−111.7	−80.5	+72	2176	852	−6948
1.00	−122.7	−122.7	352	1543	352	(*9*)
Pressure = 650 p.s.i.a.						
0	82.2	82.2	1238	3028		1238(*2*)
0.10	54.6	68.8	659	3103	5260	+148
0.20	+25.2	55.7	+149	3118	3300	−639
0.30	−3.0	42.9	−228	3080	2555	−1421
0.40	−28.3	28.9	−383	3007	2050	−2005
0.50	−51.5	+13.8	−432	2915	1620	−2484
0.60	−70.2	−4.0	−419	2792	1370	−3103
0.70	−83.0	−23.6	−263	2625	1140	−3538
0.80	−93.9	−46.8	+5	2429	1000	−3975
0.90	−105.6	−78.5	+386	2102	900	−4240
1.00	−118.0	−118.0	828	1468	828	(*9*)
Pressure = 700 p.s.i.a.						
0	88.3	88.3	1748	2620		1748(*2*)
0.10	62.5	73.6	993	2971	7491	+271
0.20	34.2	60.6	400	3002	4360	−590
0.30	+6.0	47.2	+20	2993	3053	−1280
0.40	−19.9	33.1	−198	2949	2370	−1910
0.50	−43.2	+17.4	−250	2853	1951	−2451
0.60	−62.5	−1.1	−250	2727	1511	−2891
0.70	−76.5	−20.9	−130	2563	1310	−3490
0.80	−88.2	−44.6	+139	2369	1336	−4649
0.90	−100.0	−76.5	607	1991	1819	−10,301
0.9825	−110.4	−110.4[b]	1312	1312		

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[a] $H = 0$ for pure components in ideal gas state, at unit fugacity, and 0° R. Vapor and liquid phase enthalpies of pure components obtained from literature sources cited were all adjusted to this state.

[b] Critical point.

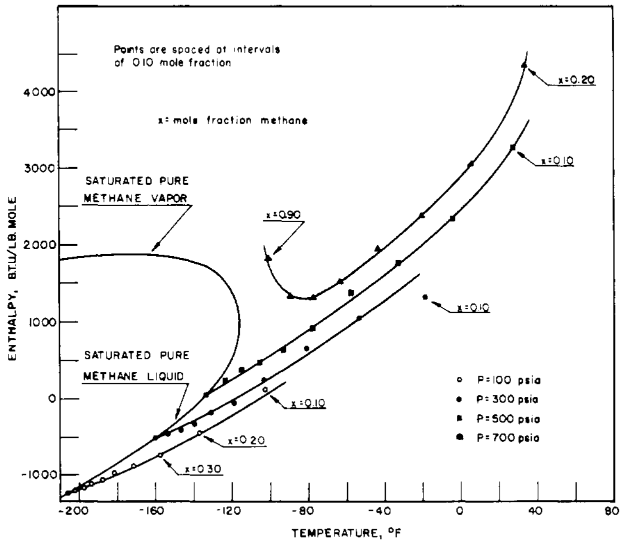

Figure 6. Partial enthalpies of ethane

Pure component data of Matthews and Hurd (9). $H = 0$ for pure methane in ideal gas state, unit fugacity, and 0° R.

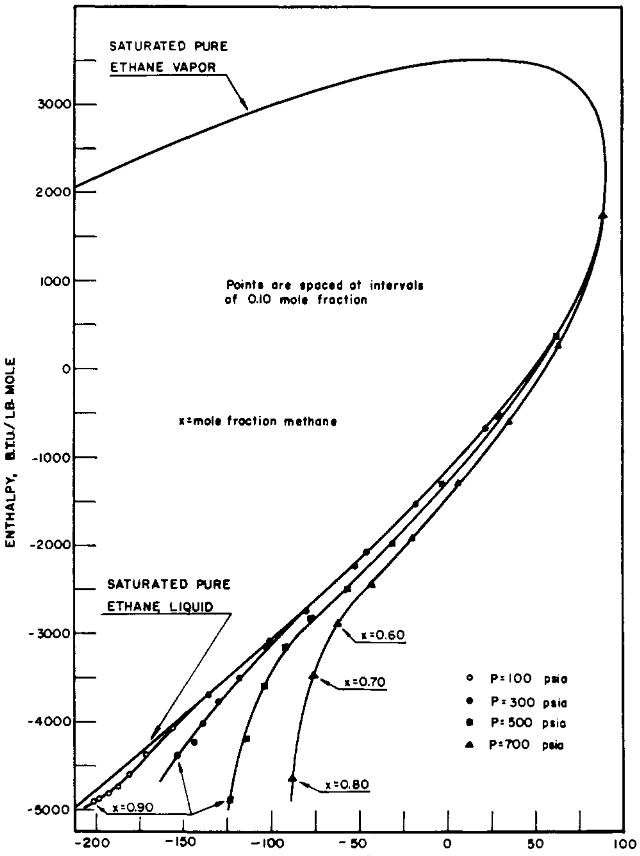

Figure 7. Partial enthalpies of ethane

Pure component data of Barkelew, Valentine, and Hurd (2) $H = 0$ for pure ethane in ideal gas state, unit fugacity, and 0° R.

ΔH_v = differential heat of vaporization, B.t.u. per lb. mole
P = pressure, p.s.i.a.
R = gas law constant, 10.731 (p.s.i.)(cu. ft.) per (lb. mole)(° R.)
T = temperature, ° R.
V = volume, cu. ft. per lb. mole
ΔV_c = volume change accompanying differential condensation process, cu. ft. per lb. mole
ΔV_v = volume change accompanying differential vaporization process, cu. ft. per lb. mole
$\bar{V}$ = partial volume, cu. ft. per lb. mole

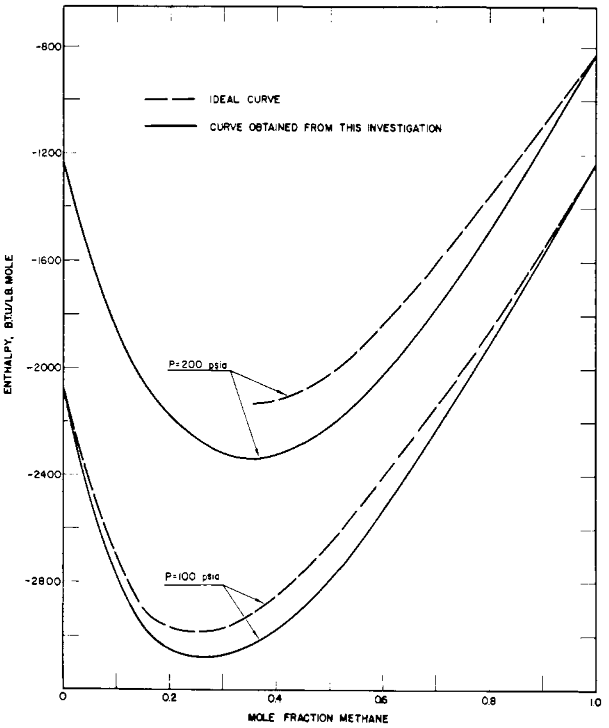

Figure 8. Ideal and actual saturated liquid phase enthalpies

a = Van der Waals attraction constant
b = Van der Waals constant, covolume
d = density, lb. moles per cu. ft.
x = mole fraction in liquid phase
y = mole fraction in vapor phase
G, ζ = quantities in Black's equation of state
$A_o, B_o, C_o, a', b', c, \alpha, \beta$ = empirical constants of Benedict-Webb-Rubin equation of state

Subscripts

G = gas phase
L = liquid phase
b = bubble point
d = dew point
i = component i in a mixture
m = mixture
l = component l in a mixture

Superscript

o = property in ideal gas state

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