Thermodynamic Properties of *N*-Propyl Alcohol

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A table of thermodynamic properties of *n*-propyl alcohol has been developed for the saturated liquid and vapor and for the superheated gas. The table was calculated on an electronic computer, using correlating equations for data from the literature on vapor pressure, pressure-volume-temperature behavior of the gas, saturated liquid density, and the ideal gas heat capacity. The results have been compared with experimental thermal data wherever possible.

THE THERMODYNAMIC properties of a pure fluid may be calculated from four items of information: (1) vapor pressure, (2) pressure–volume–temperature (P-V-T) behavior of the gas (and of the liquid if compressed liquid properties are to be determined), (3) saturated liquid density, and (4) ideal gas heat capacity. Other data such as Joule-Thompson coefficient, latent heat of vaporization, liquid heat capacity, and velocity of sound may be utilized, but if the first four items are available, the latter are usually more useful for checking. As pointed out by Cosner, Gagliardo, and Storvick (*3*), for *n*-propyl alcohol, C_3H_7OH, there are ample data of the desired kind to prepare a table of properties. Unfortunately, however, an error caused their own table of calculated entropy values to be incorrect. This effort was undertaken not only to obtain correct entropy values, but to utilize an alternate method of correlating the data and to present a more extensive table.

Two procedures are available for deriving the thermodynamic properties from the basic data: First, numerical and graphical techniques may be applied directly to the data to obtain the desired derivatives and integrals that are needed in the exact thermodynamic relations, or second, correlating empirical or semi-empirical equations may be fitted to each item of data, and the resulting equations inserted in the thermodynamic relations to be differentiated and integrated analytically. The second procedure offers an advantage in that interpolations and extrapolations can often be made with greater confidence by comparison with other compounds. Also it is simple to guarantee perfect internal consistency in this approach. Because of these advantages, the second procedure was followed in this study, while the previous effort (*3*) utilized essentially the first procedure.

THE CORRELATING EQUATIONS

P-V-T Behavior of the Gas. The data of Ramsey and Young (*16*) were fitted with an average deviation of 0.5% according to previously published methods (*11, 12*) with the following equation of state:

$$P = \frac{0.178578T}{V-b} + \frac{-20.195713 + 8.2285108 \times 10^{-3}T - 589.46586e^{-5T/T_c}}{(V-b)^2} + \frac{0.5397999 - 1.4156816 \times 10^{-5}T + 35.352704e^{-5T/T_c}}{(V-b)^3} + \frac{-1.8092567 \times 10^{-2}}{(V-b)^4} + \frac{1.8210811 \times 10^{-4} + 8.7209281 \times 10^{-8}T - 0.013960822e^{-5T/T_c}}{(V-b)^5} \quad \text{lb./sq. in.}$$

where V is in cu. ft./lb., T in °R., b = 0.00780529, and T_c = 966.33° R. The later data of Young (*19*) on the saturated vapor compared satisfactorily with the equation. Low-pressure P-V-T measurements were determined by Cox (*4*) and Foz, Morcillo, and Mendez (*6*). Data of the former investigator agree with the equation within 0.1% while data of the latter group are within about 0.4%. Second virial coefficients presented by Cox are about 3% lower than those predicted by the equation while the coefficients of Foz *et. al.* average about 5% higher than the equation. Since the data of Foz *et. al.* appear to agree better with

Table I. Saturation Properties

Temp., °F.	Pressure P.S.I.A.	Liq. Spec. Vol. Cu. Ft./Lb.	Vap. Spec. Vol. Cu. Ft./Lb.	Liq. Enthalpy B.t.u./Lb.	Vap. Enthalpy B.t.u./Lb.	Liq. Entropy B.t.u./Lb.-° R.	Vap. Entropy B.t.u./Lb.-° R.
40	0.08901	0.01967	1001.89	4.755	361.47	0.00959	0.72347
50	0.13580	0.01976	669.59	10.774	364.67	0.02152	0.71585
60	0.20323	0.01985	456.05	16.884	367.92	0.03339	0.70886
70	0.29865	0.01995	316.17	23.089	371.22	0.04521	0.70245
80	0.43139	0.02005	222.88	29.393	374.56	0.05700	0.69657
90	0.61313	0.02015	159.60	35.802	377.95	0.06877	0.69121
100	0.85821	0.02026	115.99	42.320	381.38	0.08052	0.68631
110	1.1841	0.02038	85.469	48.953	384.84	0.09226	0.68186
120	1.6115	0.02049	63.811	55.706	388.34	0.10401	0.67782
130	2.1651	0.02062	48.232	62.584	391.86	0.11577	0.67416
140	2.8735	0.02075	36.883	69.592	395.41	0.12755	0.67086
150	3.7698	0.02088	28.515	76.584	398.98	0.13936	0.66789
160	4.8916	0.02102	22.274	84.018	402.55	0.15120	0.66522
170	6.2812	0.02116	17.570	91.444	406.14	0.16308	0.66284
180	7.9861	0.02131	13.987	99.017	409.73	0.17500	0.66073
190	10.059	0.02147	11.231	106.74	413.32	0.18696	0.65886
200	12.556	0.02164	9.0925	114.61	416.91	0.19898	0.65721
207	14.696	0.02176	7.8242	120.49	419.52	0.20781	0.65612
210	15.540	0.02181	7.4180	122.64	420.47	0.21103	0.65577
220	19.078	0.02208	6.0960	130.82	424.02	0.22314	0.65451
230	23.240	0.02217	5.0440	139.15	427.55	0.23528	0.65344
240	28.103	0.02237	4.2005	147.64	431.05	0.24747	0.65252
250	33.774	0.02257	3.5194	156.28	434.51	0.25959	0.65174
260	40.248	0.02279	2.9655	165.06	437.93	0.27195	0.65109
270	27.698	0.02301	2.5123	173.99	441.31	0.28423	0.65057
280	56.183	0.02325	2.1390	183.07	444.63	0.29653	0.65014
290	65.792	0.02350	1.8298	192.28	447.90	0.30884	0.64981
300	76.615	0.02376	1.5721	201.62	451.10	0.32115	0.64956
310	88.746	0.02404	1.3562	211.09	454.24	0.33347	0.64938
320	102.27	0.02433	1.1745	220.68	457.30	0.34577	0.64925
330	117.29	0.02464	1.0206	230.38	460.28	0.35805	0.64917
340	133.90	0.02497	0.88967	240.20	463.17	0.37031	0.64913
350	152.17	0.02532	0.77778	250.12	465.96	0.38253	0.64910
360	172.22	0.02569	0.68171	260.13	468.64	0.39470	0.64907
370	194.11	0.02609	0.59883	270.24	471.20	0.40683	0.64904
380	217.95	0.02652	0.52701	280.43	473.62	0.41890	0.64898
390	243.82	0.02698	0.46449	290.69	475.90	0.43090	0.64886
400	271.82	0.02748	0.40981	301.03	477.99	0.44283	0.64868
410	302.04	0.02802	0.36177	311.45	479.89	0.45470	0.64838
420	334.58	0.02862	0.31933	321.93	481.55	0.46649	0.64794
430	369.54	0.02928	0.28164	332.49	482.93	0.47822	0.64731
440	407.21	0.03003	0.24796	343.14	483.96	0.48988	0.64641
450	447.21	0.03087	0.21761	353.89	484.55	0.50152	0.64515
460	490.23	0.03185	0.19001	364.78	484.56	0.51315	0.64339
470	536.29	0.03303	0.16454	375.89	483.75	0.52487	0.64088
480	585.69	0.03452	0.14049	387.38	481.69	0.53683	0.63719
490	638.82	0.03658	0.11674	399.65	477.40	0.54945	0.63132
500	696.35	0.04022	0.08977	414.29	467.15	0.56435	0.61943
506.64	736.09	0.05859	0.05859	441.70	441.70	0.59245	0.59245

the extrapolated data of Ramsey and Young than with Cox, there is probably a small error in the equation at lower pressures. This is borne out by later comparisons of enthalpy.

Vapor Pressure. The data of Ramsey and Young (*16*) and Mathews and McKetta (*14*), and the tabulations of Stull (*18*) and Jordan (*8*) were correlated with a high precision (*13*) equation of the form,

$$\log_{10}P = 30.798670 - (8389.2794/T) - 6.0391603\log_{10}T$$

$$-1.2771758\times10^{-3}T + [0.72646663\,(980.73 - T)/T]\times$$

$$\log_{10}(980.73- T)$$

where P is in lb./sq. in and T in °R. This equation fits that data with an average deviation of less than 0.5% everywhere except in the neighborhood of the boiling point. In this region the equation predicts pressures from 1 to 2.7% higher than Stull, 0.1 to 1.5% lower than Mathews and McKetta, and Jordan, and 1.5% higher than used by Cosner *et. al.* in their tables.

Saturated Liquid Density. The equation,

$$d_1 = 17.0667 + 50.368807\,(1 - T/T_c)^{1/3}$$

$$-76.808444\,(1 - T/T_c)^{2/3} + 164.01371\,(1 - T/T_c)$$

$$-99.398988\,(1 - T/T_c)^{4/3}\ \text{lb./cu. ft.}$$

with T in °R. and T_c as above, was fitted to the data of Ramsey and Young (*16*) and compared with the data of Antonoff (*1*). Deviations were well under a per cent except for densities a little greater than the critical where differences as much as 3 per cent were encountered. This was expected since density changes so rapidly with temperature in this region.

Heat Capacity of Ideal Gas. The equation used for the constant volume heat capacity of the ideal gas is

$$C_v = -7.143625\times10^{-2} + 8.53829\times10^{-4}T - 2.97867$$

$$\times\,10^{-7}T^2 + 4.0353446\times10^{-11}T^3\ \text{B.t.u./lb.-° R.}$$

where T is in °R. This is a modification of an equation presented by Kobe, Harrison, and Pennington (*9*) whose result was based on a statistical mechanical heat capacity using fundamental vibrational frequencies. The adjustment was made to fit the experimental data of Bennewitz and Rossner (2), Jatkar (7), Mathews and McKetta, and Sinke and DeVries (*17*). The equation predicts heat capacities 3 to 4% less than those given by Kobe *et. al.*, about 0.3 to 0.9% higher than those of Mathews and McKetta, a few tenths per cent above and below those of Sinke and DeVries, and about 3% higher than Bennewitz and Rossner. Jatkar's velocity of sound measurements are correlated well by a combination of the heat capacity equation and the *P-V-T* equation.

CALCULATION OF THE TABLES AND COMPARISON WITH THE LITERATURE

The thermodynamic properties were calculated on an IBM 7090 computer using the exact thermodynamic relations and the correlating equations given above. As shown on the Figure 1, the Tables I and II are based on setting to zero the entropy and enthalpy of the saturated liquid at 32° F. The absolute zero of temperature was taken as −459.69° F., while the gas constant was 10.7318 lb.-cu. ft./lb. mole-° R. or 1.9859 B.t.u./lb.-° R. Details of the procedure have been previously published (*10*). Because the correlating equations fit the data practically within the experimental error in all cases, it is believed that the resulting tables are of a high order of reliability.

Several comparisons should be mentioned: First, at atmospheric pressure the tables show a latent heat of vaporization of 299.036 B.t.u./lb. while Bennewitz and Rossner reported 299.0, Mathews and McKetta obtained 295.1, and Plewes, Jardine, and Butler (*15*) gave 299.9. Since the tabular value is based on the Clapeyron relation which utilizes the vapor pressure, liquid density, and *P-V-T* equations, this comparison indicates the reliability of these equations in this range, particularly because the calculated value is a good average of the experimental values. Second, one experimental investigation has been made of enthalpy changes of *n*-propanol over a range of temperature and pressure. This study was conducted by Eubank and Smith (*5*) who employed a direct calorimetric technique. In some regions their measured enthalpy changes are in good agreement with the tables presented here. In other places there is substantial disagreement, so that their results are not considered sufficiently consistent to be utilized in this work. As an example, at 300° F. they show the change of enthalpy between zero pressure and saturation pressure is 45 B.t.u./lb., while the tables given here show only 11.96 which is just about ¼ of theirs. To determine which is correct the ΔH was estimated from generalized charts of the effect of pressure on enthalpy. Several different generalized charts were used and they all showed ΔH to be about 10 B.t.u./lb. The fact that this is a little less than the tables is expected because the generalized charts are not usually based on polar compounds such as alcohols. Next the ΔH of water at the same reduced temperature and over the same reduced pressure range was converted in the usual generalized way to a predicted ΔH for *n*-propanol. This was found to be 10.11 B.t.u./;b. The experimental second virial coefficients were also used to predict the ΔH for changes of pressures up to about one-tenth the critical pressure. The coefficients given by Mathews and McKetta based on the data of Foz *et. al.* predicted $\Delta H = 12.67$ while those of Cox gave 10.64 B.t.u./lb. One can only conclude that the 11.96 given by the tables is a little low compared to the best virial coefficients, but tnat the 45 of Eubank and Smith is seriously in error. Third, Eubank and Smith also deduced latent heats of vaporization from their enthalpy measurements. At 300° F. they show ΔH_{vap} to be 228 B.t.u./lb. whereas the tables here show 249.5. If the data of Mathews and McKetta are extrapolated by use of the equation they presented but beyond their experimental range, a value of ΔH_{vap} of 249.2 is found. If the effect of temperature on the latent heat of water is generalized and applied to *n*-propanol, it is found that ΔH_{vap} should decrease by 55 B.t.u./lb. in passing from the normal boiling point to 300° F. Taking ΔH_{vap} to be 299 B.t.u./;b. at the boiling point as confirmed by experiment, the predicted ΔH_{vap} at 300° F. is 244 B.t.u./lb., which is considered good agreement with the tables. The value of 228 of Eubank and Smith must therefore be considered to be in error. Eubank and Smith made some enthalpy calculations with the *P-V-T* data of Ramsey and Young (*16*) and concluded that the *P-V-T* data must be inaccurate. Since the tables presented here are based on the data of Ramsey and Young and since the values given by Eubank and Smith have been shown to be highly improbable, it is obvious there is some difficulty. It is believed that the actual enthalpy changes measured by Eubank and Smith are fairly good, but that their analysis of data through the method of preparing their graphs is at fault. Fourth, at temperatures just below the critical the average density of the saturated liquid and vapor in the tables is not linear in temperature, which is contrary to the experimental data that show the rectilinear density line to be practically straight. This discrepancy can be attributed to the inability of the three equations above, to represent the extremely rapid changes near the critical, since it is a simultaneous solution of these equations that yields the average density. Fifth, the tabulated enthalpy values of the saturated liquid give heat capacities that are several per cent higher than those given for propyl alcohol (*iso* or normal not specified) in most handbooks. This comparison of liquid heat capacity, however, constitutes an extremely severe test of all the correlating equations, as it involves second derivatives. Consequently, differences of several per cent at the lower temperatures are not surprising.

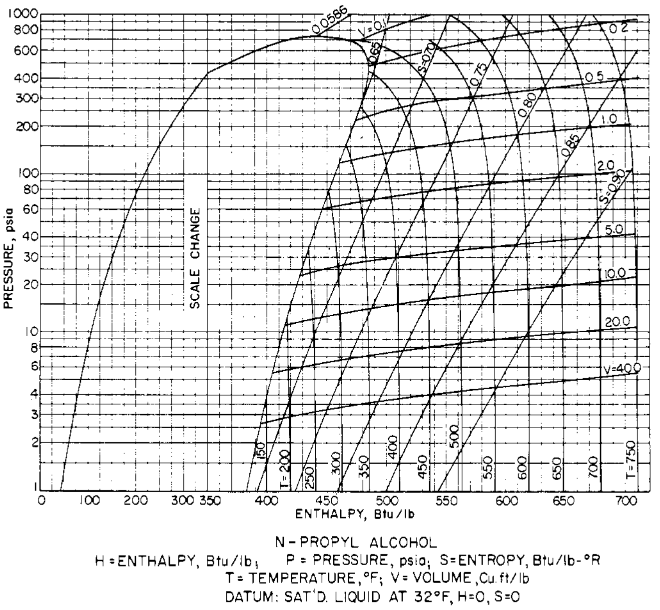

Figure 1. Thermodynamic properties of *n*-propyl alcohol

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Table II. Superheat Properties

Absolute Pressure (Sat. Temp.)

Temp., °F.	Pressure = 0			Pressure = 2 P.S.I.A.			Pressure = 4 P.S.I.A.		
	Volume Cu. Ft./Lb.	Enthalpy B.t.u./Lb.	Entropy B.t.u./Lb.-° R.	Volume Cu. Ft./Lb.	Enthalpy B.t.u./Lb.	Entropy B.t.u./Lb.-° R.	Volume Cu. Ft./Lb.	Enthalpy B.t.u./Lb.	Entropy B.t.u./Lb.-° R.
120		389.01							
140		396.41		53.161	395.67	0.68317			
160		404.02		54.985	403.34	0.69574	27.318	402.80	0.67217
180		411.84		56.805	411.21	0.70825	28.244	410.72	0.68476
200		419.88		58.620	419.29	0.72068	29.167	418.85	0.69726
220		428.12		60.431	427.57	0.73304	30.086	427.17	0.70969
240		236.56		62.240	436.05	0.74533	31.002	435.68	0.72203
260		445.20		64.046	444.72	0.75755	31.915	444.38	0.73429
280		454.03		65.850	453.58	0.76970	32.826	453.27	0.74648
300		463.06		67.652	462.63	0.78177	33.735	462.35	0.75859
320		472.27		69.452	471.87	0.79377	34.642	471.61	0.77062
340		481.67		71.250	481.29	0.80570	35.548	481.05	0.78257
360		491.26		73.047	490.89	0.81756	36.452	490.67	0.79445
380		501.02		74.843	500.67	0.82934	37.356	500.47	0.80626
400		510.95		76.638	510.62	0.84105	38.258	510.43	0.81799
420		521.06		78.433	520.74	0.85269	39.159	520.57	0.82964
440		531.34		80.226	531.03	0.86426	40.059	530.87	0.84122
460		541.79		82.019	541.48	0.87575	40.959	541.33	0.85273
480		552.39		83.811	552.10	0.88717	41.858	551.96	0.86416
500		563.16		85.602	562.88	0.89852	42.757	562.75	0.87551
520		574.09		87.393	573.81	0.90980	43.644	574.69	0.88680
540		585.17		89.184	584.90	0.92100	44.553	584.78	0.89801
560		596.40		90.974	596.14	0.93213	45.450	596.03	0.90915
580		607.78					46.347	607.42	0.92021
600		619.31					47.244	618.96	0.93120
	Pressure = 8 P.S.I.A.			Pressure = 20 P.S.I.A.			Pressure = 40 P.S.I.A.		
200	14.439	417.95	0.67332						
220	14.912	426.35	0.68587						
240	15.382	434.94	0.69832	6.0054	432.65	0.66553			
260	15.849	443.71	0.71067	6.2057	441.63	0.67818	2.9854	437.98	0.65135
280	16.314	452.66	0.72294	6.4034	450.77	0.69071	3.0954	447.47	0.66436
300	16.776	461.79	0.73512	6.5989	460.07	0.70310	3.2027	457.07	0.67717
320	17.237	471.10	0.74721	6.7924	469.52	0.71539	3.3079	466.80	0.68980
340	17.697	480.58	0.75922	6.9843	479.13	0.72756	3.4112	476.65	0.70228
360	18.155	490.24	0.77114	7.1747	488.81	0.73963	3.5129	486.63	0.71461
380	18.611	500.06	0.78299	7.3640	498.84	0.75160	3.6133	496.75	0.72680
400	19.067	510.06	0.79475	7.5521	508.93	0.76348	3.7125	507.00	0.73887
420	19.522	520.22	0.80644	7.7392	519.18	0.77526	3.8106	517.40	0.75082
440	19.976	530.55	0.81805	7.9256	529.58	0.78695	3.9079	527.93	0.76266
460	20.429	541.04	0.92958	8.1112	540.14	0.79856	4.0044	538.61	0.77440
480	20.882	551.68	0.84103	8.2961	550.85	0.81008	4.1002	549.43	0.78603
500	21.334	562.49	0.85241	8.4805	561.71	0.82151	4.1954	560.38	0.79757
520	21.786	573.45	0.86371	8.6644	572.71	0.83287	4.2901	571.48	0.80901
540	22.237	584.56	0.87493	8.8478	583.87	0.84414	4.3844	582.71	0.82036
560	22.688	595.82	0.88608	9.0309	595.17	0.85533	4.4782	594.08	0.83163
580	23.139	607.22	0.89716	9.2135	606.61	0.86644	4.5716	605.59	0.84280
600	23.589	618.77	0.90816	9.3959	618.20	0.87748	4.6648	617.23	0.85389
	Pressure = 60 P.S.I.A.			Pressure = 100 P.S.I.A.			Pressure = 200 P.S.I.A.		
300	2.0672	453.90	0.66052						
320	2.1437	463.93	0.67356	1.2060	457.68	0.65038			
340	2.2180	474.05	0.68637	1.2587	468.45	0.66403			
360	2.2906	484.27	0.69899	1.3091	479.22	0.67732			
380	2.3617	494.59	0.71143	1.3576	490.02	0.69033	0.5925	476.52	0.65464
400	2.4315	505.02	0.72371	1.4045	500.86	0.70310	0.6253	488.89	0.66920
420	2.5002	515.58	0.73584	1.4501	511.77	0.71564	0.6557	501.05	0.68318
440	2.5680	526.25	0.74784	1.4946	522.75	0.72799	0.6843	513.07	0.69670
460	2.6349	537.05	0.75972	1.5381	533.83	0.74016	0.7115	825.03	0.70984
480	2.7011	547.98	0.77147	1.5809	545.00	0.75218	0.7375	536.95	0.72266
500	2.7667	559.04	0.78311	1.6229	556.27	0.76405	0.7626	548.88	0.73522
520	2.8317	570.22	0.79465	1.6644	567.65	0.77578	0.7869	560.82	0.74754
540	2.8963	581.54	0.80608	1.7053	579.14	0.78739	0.8105	572.81	0.75966
560	2.9604	592.98	0.81742	1.7458	590.74	0.79888	0.8336	584.86	0.77159
580	3.0242	604.56	0.82866	1.7859	602.45	0.81026	0.8561	596.97	0.78335
600	3.0876	616.26	0.83981	1.8256	614.28	0.82153	0.8783	609.15	0.79495
	Pressure = 400 P.S.I.A.			Pressure = 800 P.S.I.A.			Pressure = 1400 P.S.I.A.		
440	0.2566	485.41	0.64838						
460	0.2831	501.78	0.66638						
480	0.3052	516.77	0.68251						
500	0.3246	531.02	0.69751						
520	0.3423	544.81	0.71174	0.0787	472.80	0.62360	0.0338	406.13	0.55112
540	0.3588	558.31	0.72538	0.1145	511.55	0.66283	0.0369	431.01	0.57627
560	0.3742	571.62	0.73856	0.1336	533.96	0.68502	0.0409	454.82	0.59985
580	0.3888	584.80	0.75137	0.1482	552.71	0.70324	0.0472	480.73	0.62501
600	0.4028	597.91	0.76385	0.1605	569.76	0.71949	0.0568	509.01	0.65195

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Vapor-Liquid Equilibrium Constants at Infinite Dilution Determined by Gas Chromatography: Ethane, Propane, and *N*-Butane in the Methane-Decane System

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The gas chromatography technique has been extended to determine the *K*-values of ethane, propane, and *n*-butane at infinite dilution in the methane-decane system at 70, 40, 0, and −20° F. from near atmospheric pressure to 2000 p.s.i. The *K*-value of *n*-butane at infinite dilution in the methane-decane system has also been measured at 160° F. from near atmospheric pressure to 460 p.s.i.

GAS-LIQUID partition chromatography (GLPC) has been used to determine vapor-liquid equilibrium data under certain conditions by several investigators. Porter, Deal, and Stross (*9*), Anderson (*2*), and Anderson and Napier (*1*) found substantial agreement between partition coefficients determined by gas-liquid chromatography and those obtained from static methods of measurement. Several authors (*7, 13*) have calculated activity coefficients from GLPC elution data and found these values in agreement with values measured by static means. These previous studies were conducted at near atmospheric pressure using an elution gas such as nitrogen, hydrogen, or helium that was insoluble in the particular non-volatile liquid phase considered. The partition coefficients so determined were for the solute at essentially infinite dilution in a one component liquid phase.

In the work described in this paper the technique of gas-liquid chromatography has been extended to determine over a wide range of pressure and temperature the equilibrium K or y/x values of a solute at essentially infinite dilution in a vapor-liquid system in which the liquid phase contains appreciable quantities of two components, one essentially non-volatile. In particular, the K values of ethane, propane, and n-butane at infinite dilution in the methane-decane system have been measured at 70, 40, 0, and −20° F. from near atmospheric pressure to 2000 p.s.i. The K-value of n-butane at infinite dilution in the methane-decane system has also been measured at 160° F. from near atmospheric pressure to 460 p.s.i.

EXPERIMENTAL PROCEDURE

The apparatus used is similar to a conventional gas-liquid chromatograph except that it has been modified for the packed column to operate at high pressures. Tubing, valves, and fittings are of stainless steel with all connections for ⅛ inch stock to minimize dead space.

A vapor solute sample was introduced by diverting the high pressure elution gas flow through a sample tube. A Wilkens six port linear sample valve accomplished the sample introduction. O-rings fitted on a sliding stem partitioned off various parts of the valve body. Depending on whether the stem was in the up or down position, gas flow was either straight through the valve or diverted through the sample tube. The sample introduction valve was located outside the liquid temperature bath in which the GLPC column was immersed, since small, abrasive particles in the bath kept working past the stem to damage the O-rings.

Pressure regulation in the GLPC column was achieved with a sensitive diaphragm regulator placed just upstream from the sample introduction valve. Flow rate through the column and reference side of the system was controlled

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