

Table and Mollier Chart of the Thermodynamic Properties of 1, 3-Butadiene*

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This paper contains a working table and Mollier chart of the thermodynamic properties of 1, 3-butadiene in engineering units, for which the data were calculated from a set of empirical equations. These equations have been published elsewhere and shown to be consistent with exact thermodynamic relations and to represent the observed data within the limits of the experimental accuracy. The table covers the properties of the saturated fluid over the temperature range extending from the triple point (-164.05°F) to within 20 degrees of the critical temperature (305.6°F). Examples are solved to illustrate the use of the table and Mollier chart ($\log P$ versus H). Several other charts are also presented.

I. Introduction

The extensive use of butadiene in the production of synthetic rubber led to a need for more complete and more accurate data on the properties of this substance than were available when it acquired commercial and military importance. Letter Circular LC710, a collection of the available data at the time, was published in December 1942. Further need developed for tables of liquid densities of butadiene and other C_4 hydrocarbons found in commercial C_4 mixtures, for the purpose of computing, from observed volumes, the quantities of materials bought or sold. This problem was brought to the National Bureau of Standards in July 1943, by representatives of the Rubber Reserve Company. Letter Circular LC 736, containing tables of liquid densities of eleven hydrocarbons found in commercial C_4 mixtures, was prepared from data available in the literature and issued in November 1943. The need for more extensive tables of the thermodynamic properties of butadiene led to a program of experimental work at the National Bureau of Standards to supply the data. The results of these measurements were published in 1945 in Research Papers RP1640 and RP1661. The present paper gives the data in the customary engineering units in the more useful form of an extensive table and a Mollier chart.

II. Experimental Data

The experimental data upon which these tables are based are those given in two recent publications [7, 8]¹. These publications describe the results of measurements made on butadiene at the National Bureau of Standards, compare them with the relatively small amount of data available from other laboratories, and develop empirical equations that are consistent with exact thermodynamic relations and that represent the observed data within the limit of experimental accuracy, which for P-V-T data on the vapor is one to three parts per thousand, for density of the liquid a very few parts in ten thousand, and for the excess of the enthalpy or entropy over that for the solid at the triple point is approximately one part per thousand. This limit is probably as small as is practicable in view of the rather unstable character of the material that polymerizes to some extent, even while observations are in progress.

Other publications [1, 2] were consulted, and the data they contained were used for comparison and verification, but not to any considerable extent as source data for the tables. The temperature of the triple point was taken as -164.05°F (-108.92°C), that of the boiling point as 24.06°F (-4.41°C), and that of the critical point as 305.6°F (152°C). The value for the critical point is believed to be reliable to one or two $^{\circ}\text{C}$. Poly-

* This paper was also published as a Technical Report to the Office of Rubber Reserve, June 30, 1947.

¹ Figures in brackets indicate the literature references at the end of this paper.

merization occurring before and during the observations limited the accuracy of the determination of the critical temperature.

III. Notation

In general, the abbreviations approved as American Tentative Standard (ASA Z101-1932) have been used, with the exception that in giving numerical values of temperatures, the degree sign ($^{\circ}$) has been retained. The units and symbols used are listed in table 1.

TABLE 1.—Units and notation

Quantity	Unit	Symbol	Formula
Pressure.....	lb/in. ²	<i>P</i>	
Specific volume.....	ft ³ /lb.....	<i>v</i>	
Temperature.....	$^{\circ}$ F.....	<i>t</i>	
Absolute temperature.....	$^{\circ}$ R.....	<i>T</i>	$T=t+459.688.$
Heat added.....	Btu/lb.....	<i>q</i>	
Internal energy.....	do.....	<i>u</i>	$^a du=dq-pdv.$
Enthalpy (heat content).....	do.....	<i>h</i>	$^a h=u+pv.$
Entropy.....	Btu/lb $^{\circ}$ R.....	<i>s</i>	$ds=dq/T.$
Latent heat of vaporization.....	Btu/lb.....	<i>h_{fg}</i>	$h_{fg}=h_g-h_f.$

SUBSCRIPTS

Property of liquid.....	<i>f</i>
Property of vapor.....	<i>g</i>
Transition from liquid to vapor.....	<i>fg</i>

^a The factor 1 (ft³) (lb/in.²) = 0.185052 Btu is necessary for numerical calculations in engineering units.

IV. Fundamental Units and Constants

1. Temperature Scale

The Fahrenheit scale used in these tables is derived from the international temperature scale [3] of 1927 by means of the relation:

$$\text{Fahrenheit temperature} = 1.8 \times \text{centigrade temperature} + 32.$$

It is not expected that any changes that may be made when the pending revision of the scale of 1927 is adopted, will require any material change in the numerical values of temperatures as given in these tables.

Temperatures on the absolute Fahrenheit scale were obtained by adding 459.688 $^{\circ}$ to the temperatures as defined above.

2. Heat Units

All of the calorimetric measurements were made in terms of the international joule, which was therefore the fundamental heat unit. It is based upon the standards of resistance and electromotive force maintained at the Bureau and upon the mean solar second. The relation between the international joule and the corresponding cgs units, according to the most recent data [4] is:

$$1 \text{ international joule} = 1.00017 \text{ absolute joules.}$$

In the thermodynamic equations relations occur between quantities of energy, some of which were measured in international joules, whereas others such as the product of pressure and volume each expressed in appropriate units, were measured directly in mechanical units, that is, absolute joules. Although the difference might be considered of negligible importance, it was taken into account where it could have any appreciable effect on the results obtained.

As secondary heat units the calorie and the British thermal unit (Btu) have been used. The calorie is the International Table (IT) calorie, widely used in engineering tables of the properties of steam. It was officially adopted by the second International Steam Table conference [5] held in London in 1929, and is defined as 3,600/860 (approximately 4.1860) international joules. In this way the mechanical equivalent of heat, so significant in earlier tables, loses its importance as it becomes a defined rather than an experimental constant and therefore is in no way dependent upon the results of past or future measurements of the properties of water.

The Btu used is derivable from the calorie by use of relations that depend only upon the relative sizes of the centigrade and Fahrenheit degrees, and the relation between the kilogram and the pound thus,

$$1 \text{ Btu} = 453.592 \times \frac{5}{9} = 251.996 \text{ IT calories} = 1054.866 \text{ int joules.}$$

This method of defining the Btu retains the convenient relation

$$1 \text{ calorie per gram} = 1.8 \text{ Btu per pound.}$$

3. Relations Between Energy Units

The relation between the Btu defined above, and the standard foot-pound is $1 \text{ Btu} = 1054.866 \text{ int joules}$
$$\times \frac{10^7 \times 0.3937}{980.665 \times 453.592 \times 12} = 778.160 \text{ ft lb.}$$

In using the tables, quantities of heat or work that are given in Btu may be converted into foot-pounds by multiplying by the factor 778.160. In cases where the reverse conversion is desired, the relation may be written,

$$1 \text{ ft-lb} = 0.00128508 \text{ Btu.}$$

As volumes are given in ft^3 and pressures in lb/in.^2 , the relation $1 (\text{ft}^3) (\text{lb/in.}^2) = 144 (0.00128508) = 0.185052 \text{ Btu}$ becomes necessary wherever numerical values are given in an equation involving both energy in Btu and the product pv in British engineering units.

4. Units of Pressure

In the British system the unit of force is the pound weight, which becomes definite when the value of the acceleration due to gravity is specified. The value used here is $980.665 \text{ cm/sec}^{-2}$.²

The unit of pressure used in this publication is one standard pound weight per sq in. absolute. The lower pressures have been expressed also in inches of mercury with use of the factor,

$$1 \text{ lb/in.}^2 = 2.03601 \text{ in Hg.}$$

² In 1901 the International Committee of Weights and Measures recommended the adoption of an experimental value 980.665 cm/sec^2 (32.174 ft/sec^2) as the value of gravity at latitude 45° and sea level [5]. Since then, those who have occasion to use a standard value for g have been divided into two groups, one of which uses the current "best" value for g at latitude 45° and sea level. The current value is about 980.62 cm/sec^2 . The other group has loyally followed the lead of the international committee in using 980.665 cm/sec^2 . The value 980.665 cm/sec^2 has been used in computing these tables.

5. Units of Volume and Density

The volumetric apparatus was calibrated either with water or with mercury. The volume unit was defined by the relations:

One cm^3 of water at 4°C under 1 atm pressure has a mass of 0.999973 g. One ml of water at 4°C under 1 atm pressure has a mass of 1.000000 grams. One cm^3 of mercury at 0°C under 1 atm pressure has a mass of 13.5951 g. Densities measured in g/ml were converted by means of the relation [4],

$$1 \text{ g/ml} = 62.42658 \text{ lb/ft}^3.$$

V. Description of Table

Only the properties of the saturated fluid have been tabulated. These are presented in table 2, which uses the notation described in the preceding section and in which the argument is temperature. The table covers the whole temperature range from the triple point -164.05°F to the critical temperature 305.6°F . Values are given every degree Fahrenheit in the temperature range 0° to 200°F and at less frequent intervals outside this range. Such arrangement gives a table with an ample number of entries in the portion most used, and keeps the table within a reasonable size. The pressures are absolute and for the lower temperatures are given in two units, namely lb/in.^2 and inches Hg at 32°F . The next two columns are devoted to the specific volume of liquid and vapor respectively in ft^3/lb . In that portion of the table where only one column of pressures is given, a column of densities of the vapor in lb/ft^3 has been inserted so that the table contains the same number of columns throughout.

TABLE 2.—Properties of saturated 1, 3-butadiene

Temperature, <i>t</i>	Abs. pressure		Specific volume <i>v</i>		Enthalpy			Entropy		Temperature, <i>t</i>
	<i>p</i>	<i>p</i>	Liquid, <i>v_f</i>	Vapor, <i>v_g</i>	Liquid, <i>h_f</i>	Evap., <i>h_{fg}</i>	Vapor, <i>h_g</i>	Liquid, <i>s_f</i>	Vapor, <i>s_g</i>	
°F	lb/in. ²	in. Hg	ft ³ /lb	ft ³ /lb	Btu/lb	Btu/lb	Btu/lb	Btu/lb°R	Btu/lb°R	°F
Triple point	0.010	Solid	5.706	5.706	59.14	282.7	341.8	0.3757	1.3317	-164.05
	.010	Liquid	0.020972	5.706	122.61	219.2	341.8	.5904	1.3317	-164.05
-160	.013	0.027	.021036	4.504	124.44	218.3	342.7	.5973	1.3256	-160
-155	.018	.037	.021117	3,310	126.71	217.1	343.8	.6048	1.3174	-155
-150	.025	.051	.021198	2,461	128.98	216.0	345.0	.6122	1.3096	-150
-145	.034	.069	.021279	1,850	131.26	214.8	346.1	.6195	1.3023	-145
-140	.045	.092	.021362	1,406	133.55	213.7	347.3	.6267	1.2953	-140
-135	.060	.121	.021446	1,079.6	135.83	212.6	348.4	.6338	1.2886	-135
-130	.078	.159	.021530	836.8	138.13	211.5	349.6	.6408	1.2823	-130
-125	.101	.206	.021615	654.6	140.42	210.4	350.8	.6478	1.2764	-125
-120	.130	.265	.021701	516.5	142.72	209.3	352.0	.6546	1.2707	-120
-115	.166	.338	.021787	411.0	145.03	208.2	353.2	.6613	1.2654	-115
-110	.210	.428	.021876	329.6	147.33	207.1	354.5	.6680	1.2603	-110
-105	.264	.537	.021964	266.3	149.65	206.1	355.7	.6745	1.2555	-105
-100	.329	.669	.022054	216.7	151.96	205.0	356.9	.6810	1.2509	-100
-95	.407	.828	.022144	177.6	154.29	203.9	358.2	.6874	1.2466	-95
-90	.500	1.017	.022236	146.4	156.61	202.9	359.5	.6938	1.2425	-90
-85	.610	1.242	.022328	121.52	158.95	201.8	360.8	.7000	1.2386	-85
-80	.740	1.507	.022420	101.44	161.29	200.8	362.0	.7062	1.2350	-80
-75	.893	1.817	.022511	85.16	163.63	199.7	363.3	.7124	1.2315	-75
-70	1.071	2.180	.022606	71.88	165.99	198.7	364.7	.7184	1.2283	-70
-65	1.277	2.600	.022702	60.98	168.35	197.6	366.0	.7245	1.2252	-65
-60	1.516	3.086	.022799	52.00	170.72	196.6	367.3	.7304	1.2223	-60
-58	1.621	3.300	.022838	48.85	171.67	196.2	367.8	.7328	1.2212	-58
-56	1.732	3.526	.022878	45.93	172.62	195.8	368.4	.7352	1.2201	-56
-54	1.849	3.765	.022917	43.21	173.57	195.3	368.9	.7375	1.2190	-54
-52	1.973	4.017	.022957	40.68	174.53	194.9	369.5	.7399	1.2180	-52
-50	2.103	4.283	.022997	38.33	175.49	194.5	370.0	.7422	1.2170	-50
-48	2.241	4.563	.023037	36.14	176.44	194.1	370.5	.7445	1.2160	-48
-46	2.386	4.857	.023077	34.10	177.40	193.7	371.1	.7469	1.2150	-46
-44	2.538	5.167	.023118	32.19	178.36	193.3	371.6	.7492	1.2141	-44
-42	2.698	5.494	.023158	30.41	179.33	192.8	372.2	.7515	1.2132	-42
-40	2.867	5.836	.023199	28.75	180.29	192.4	372.7	.7538	1.2123	-40
-38	3.043	6.196	.023240	27.20	181.26	192.0	373.3	.7561	1.2114	-38
-36	3.229	6.574	.023281	25.74	182.23	191.6	373.8	.7584	1.2105	-36
-34	3.423	6.970	.023323	24.38	183.19	191.2	374.4	.7606	1.2097	-34
-32	3.627	7.386	.023364	23.10	184.16	190.7	374.9	.7629	1.2089	-32
-30	3.841	7.821	.023406	21.91	185.14	190.3	375.5	.7652	1.2081	-30
-28	4.065	8.277	.023448	20.79	186.11	189.9	376.0	.7674	1.2074	-28
-26	4.299	8.754	.023491	19.73	187.09	189.5	376.6	.7697	1.2066	-26
-24	4.544	9.252	.023533	18.74	188.06	189.1	377.1	.7719	1.2059	-24
-22	4.801	9.774	.023576	17.81	189.04	188.6	377.7	.7742	1.2052	-22
-20	5.068	10.319	.023619	16.94	190.02	188.2	378.2	.7764	1.2045	-20
-18	5.348	10.888	.023662	16.11	191.01	187.8	378.8	.7786	1.2038	-18
-16	5.639	11.482	.023705	15.34	191.99	187.4	379.4	.7809	1.2032	-16
-14	5.944	12.102	.023749	14.61	192.98	186.9	379.9	.7831	1.2025	-14
-12	6.261	12.748	.023793	13.92	193.97	186.5	380.5	.7853	1.2019	-12
-10	6.592	13.421	.023837	13.27	194.96	186.1	381.0	.7875	1.2013	-10
-8	6.937	14.123	.023882	12.66	195.95	185.7	381.6	.7897	1.2007	-8
-6	7.295	14.854	.023926	12.08	196.94	185.2	382.2	.7919	1.2002	-6
-4	7.669	15.614	.023971	11.53	197.94	184.8	382.7	.7941	1.1996	-4
-2	8.057	16.405	.024016	11.01	198.94	184.4	383.3	.7963	1.1991	-2
0	8.461	17.23	.024062	10.525	199.94	183.9	383.9	.7984	1.1985	0
1	8.669	17.65	.024084	10.290	200.44	183.7	384.2	.7995	1.1983	1
2	8.881	18.08	.024107	10.062	200.94	183.5	384.4	.8006	1.1980	2
3	9.097	18.52	.024130	9.839	201.44	183.3	384.7	.8017	1.1978	3
4	9.317	18.97	.024153	9.623	201.94	183.1	385.0	.8028	1.1976	4

TABLE 2.—*Properties of saturated 1, 3-butadiene—Continued*

Temperature, <i>t</i>	Abs. pressure		Specific volume		Enthalpy			Entropy		Temperature, <i>t</i>
	<i>p</i>	<i>p</i>	Liquid, <i>v_f</i>	Vapor, <i>v_g</i>	Liquid, <i>h_f</i>	Evap., <i>h_{fg}</i>	Vapor, <i>h_g</i>	Liquid, <i>s_f</i>	Vapor, <i>s_g</i>	
°F	lb/in. ²	in. Hg	ft ³ /lb	ft ³ /lb	Btu/lb	Btu/lb	Btu/lb	Btu/lb°R	Btu/lb°R	°F
5	9.542	19.43	0.024176	9.413	202.44	182.8	385.3	0.8038	1.1973	5
6	9.770	19.89	.024199	9.208	202.95	182.6	385.6	.8049	1.1971	6
7	10.003	20.37	.024223	9.008	203.45	182.4	385.9	.8060	1.1969	7
8	10.241	20.85	.024246	8.814	203.96	182.2	386.1	.8071	1.1966	8
9	10.482	21.34	.024269	8.625	204.47	182.0	386.4	.8082	1.1964	9
10	10.728	21.84	.024293	8.441	204.97	181.7	386.7	.8092	1.1962	10
11	10.979	22.35	.024316	8.261	205.48	181.5	387.0	.8103	1.1960	11
12	11.234	22.87	.024340	8.087	205.98	181.3	387.3	.8114	1.1957	12
13	11.494	23.40	.024363	7.917	206.49	181.1	387.6	.8125	1.1955	13
14	11.759	23.94	.024387	7.751	207.00	180.9	387.9	.8135	1.1953	14
15	12.029	24.49	.024411	7.589	207.50	180.6	388.1	.8146	1.1951	15
16	12.303	25.05	.024435	7.431	208.01	180.4	388.4	.8157	1.1949	16
17	12.582	25.62	.024459	7.278	208.52	180.2	388.7	.8167	1.1947	17
18	12.866	26.20	.024483	7.128	209.03	180.0	389.0	.8178	1.1945	18
19	13.155	26.78	.024507	6.982	209.54	179.7	389.3	.8189	1.1943	19
20	13.45	27.38	.024531	6.840	210.05	179.5	389.6	.8199	1.1942	20
21	13.75	27.99	.024555	6.701	210.57	179.3	389.9	.8210	1.1940	21
22	14.05	28.61	.024579	6.566	211.08	179.1	390.1	.8220	1.1938	22
23	14.36	29.24	.024604	6.434	211.59	178.8	390.4	.8231	1.1936	23
24	14.68	29.88	.024628	6.305	212.10	178.6	390.7	.8242	1.1934	24
25	15.00	30.54	.024653	6.179	212.62	178.4	391.0	.8252	1.1933	25
26	15.32	31.20	.024677	6.057	213.13	178.2	391.3	.8263	1.1931	26
27	15.66	31.87	.024702	5.937	213.65	177.9	391.6	.8273	1.1929	27
28	15.99	32.56	.024727	5.820	214.16	177.7	391.9	.8284	1.1928	28
29	16.34	33.26	.024752	5.706	214.68	177.5	392.2	.8294	1.1926	29
30	16.68	33.97	.024777	5.595	215.19	177.2	392.4	.8305	1.1925	30
31	17.04	34.69	.024802	5.487	215.71	177.0	392.7	.8316	1.1923	31
32	17.40	35.42	.024827	5.381	216.23	176.8	393.0	.8326	1.1921	32
33	17.76	36.17	.024852	5.277	216.75	176.6	393.3	.8337	1.1920	33
34	18.13	36.92	.024877	5.176	217.27	176.3	393.6	.8347	1.1919	34
35	18.51	37.69	.024903	5.077	217.79	176.1	393.9	.8357	1.1917	35
36	18.90	38.47	.024928	4.981	218.31	175.9	394.2	.8368	1.1916	36
37	19.29	39.27	.024954	4.887	218.83	175.6	394.5	.8378	1.1914	37
38	19.68	40.07	.024979	4.795	219.35	175.4	394.7	.8389	1.1913	38
39	20.08	40.89	.025005	4.705	219.87	175.2	395.0	.8399	1.1912	39
40	20.49	41.72	.025031	4.617	220.40	174.9	395.3	.8410	1.1910	40
41	20.91	42.57	.025057	4.531	220.92	174.7	395.6	.8420	1.1909	41
42	21.33	43.43	.025083	4.447	221.44	174.4	395.9	.8431	1.1908	42
43	21.76	44.30	.025109	4.365	221.97	174.2	396.2	.8441	1.1907	43
44	22.19	45.19	.025135	4.285	222.50	174.0	396.5	.8451	1.1905	44
45	22.63	46.08	.025161	4.207	223.02	173.7	396.8	.8462	1.1904	45
46	23.08	47.00	.025188	4.130	223.55	173.5	397.0	.8472	1.1903	46
47	23.54	47.92	.025214	4.055	224.08	173.3	397.3	.8483	1.1902	47
48	24.00	48.86	.025241	3.982	224.61	173.0	397.6	.8493	1.1901	48
49	24.47	49.82	.025267	3.911	225.13	172.8	397.9	.8503	1.1900	49

TABLE 2.—Properties of saturated 1, 3-butadiene—Continued

Temperature, <i>t</i>	Abs. pressure	Specific volume		Density vapor $1/v_g$	Enthalpy			Entropy		Temperature, <i>t</i>
		v_f	v_g		Liquid h_f	Evap. h_{fg}	Vapor h_g	Liquid s_f	Vapor s_g	
$^{\circ}F$	lb/in. ²	ft ³ /lb	ft ³ /lb	lb/ft ³	Btu/lb	Btu/lb	Btu/lb	Btu/lb ^o R	Btu/lb ^o R	$^{\circ}F$
50	24.94	0.025294	3.840	0.2604	225.66	172.5	398.2	0.8514	1.1899	50
51	25.43	.025321	3.772	.2651	226.19	172.3	398.5	.8524	1.1898	51
52	25.92	.025348	3.705	.2699	226.72	172.1	398.8	.8534	1.1897	52
53	26.42	.025375	3.639	.2748	227.26	171.8	399.1	.8545	1.1896	53
54	26.92	.025402	3.575	.2797	227.79	171.6	399.4	.8555	1.1895	54
55	27.43	.025429	3.512	.2847	228.32	171.3	399.6	.8565	1.1894	55
56	27.95	.025456	3.451	.2898	228.85	171.1	399.9	.8575	1.1893	56
57	28.48	.025484	3.391	.2949	229.39	170.8	400.2	.8586	1.1892	57
58	29.01	.025511	3.332	.3001	229.93	170.6	400.5	.8596	1.1891	58
59	29.56	.025539	3.275	.3054	230.46	170.3	400.8	.8607	1.1891	59
60	30.11	.025567	3.218	.3107	231.00	170.1	401.1	.8617	1.1890	60
61	30.66	.025595	3.163	.3162	231.53	169.8	401.4	.8627	1.1889	61
62	31.23	.025623	3.109	.3217	232.07	169.6	401.7	.8637	1.1888	62
63	31.80	.025651	3.056	.3272	232.61	169.3	401.9	.8648	1.1887	63
64	32.39	.025679	3.004	.3329	233.15	169.1	402.2	.8658	1.1887	64
65	32.97	.025707	2.954	.3386	233.69	168.8	402.5	.8668	1.1886	65
66	33.57	.025736	2.904	.3444	234.23	168.6	402.8	.8678	1.1885	66
67	34.18	.025764	2.855	.3502	234.77	168.3	403.1	.8689	1.1885	67
68	34.79	.025793	2.808	.3562	235.31	168.1	403.4	.8699	1.1884	68
69	35.42	.025821	2.761	.3622	235.85	167.8	403.7	.8709	1.1883	69
70	36.05	.025850	2.715	.3683	236.40	167.6	404.0	.8719	1.1883	70
71	36.69	.025879	2.670	.3745	236.94	167.3	404.2	.8730	1.1882	71
72	37.34	.025908	2.626	.3808	237.49	167.0	404.5	.8740	1.1882	72
73	37.99	.025938	2.583	.3871	238.03	166.8	404.8	.8750	1.1881	73
74	38.66	.025967	2.541	.3935	238.58	166.5	405.1	.8760	1.1880	74
75	39.33	.025996	2.500	.4001	239.13	166.3	405.4	.8770	1.1880	75
76	40.02	.026026	2.459	.4066	239.68	166.0	405.7	.8780	1.1879	76
77	40.71	.026056	2.419	.4133	240.23	165.7	406.0	.8791	1.1879	77
78	41.41	.026085	2.380	.4201	240.77	165.5	406.3	.8801	1.1879	78
79	42.12	.026115	2.342	.4269	241.32	165.2	406.5	.8811	1.1878	79
80	42.84	.026145	2.305	.4339	241.88	165.0	406.8	.8821	1.1878	80
81	43.57	.026176	2.268	.4409	242.43	164.7	407.1	.8831	1.1877	81
82	44.31	.026206	2.232	.4480	242.98	164.4	407.4	.8841	1.1877	82
83	45.06	.026236	2.197	.4552	243.53	164.2	407.7	.8852	1.1876	83
84	45.82	.026267	2.162	.4625	244.09	163.9	408.0	.8862	1.1876	84
85	46.59	.026298	2.128	.4699	244.64	163.6	408.3	.8872	1.1876	85
86	47.36	.026328	2.095	.4773	245.20	163.4	408.5	.8882	1.1875	86
87	48.15	.026359	2.062	.4849	245.75	163.1	408.8	.8892	1.1875	87
88	48.95	.026391	2.030	.4926	246.31	162.8	409.1	.8902	1.1875	88
89	49.75	.026422	1.999	.5003	246.87	162.5	409.4	.8912	1.1875	89
90	50.57	.026453	1.968	.5082	247.43	162.3	409.7	.8922	1.1874	90
91	51.40	.026485	1.938	.5161	247.99	162.0	410.0	.8933	1.1874	91
92	52.23	.026516	1.908	.5242	248.55	161.7	410.3	.8943	1.1874	92
93	53.08	.026548	1.879	.5323	249.11	161.4	410.5	.8953	1.1874	93
94	53.94	.026580	1.850	.5405	249.67	161.2	410.8	.8963	1.1873	94
95	54.81	.026612	1.822	.5489	250.23	160.9	411.1	.8973	1.1873	95
96	55.68	.026644	1.794	.5573	250.80	160.6	411.4	.8983	1.1873	96
97	56.57	.026677	1.767	.5658	251.36	160.3	411.7	.8993	1.1873	97
98	57.47	.026709	1.741	.5745	251.93	160.0	412.0	.9003	1.1873	98
99	58.38	.026742	1.715	.5832	252.49	159.8	412.3	.9013	1.1873	99
100	59.30	.026775	1.689	.5921	253.0	159.5	412.5	.9023	1.1872	100
101	60.24	.026808	1.664	.6010	253.6	159.2	412.8	.9033	1.1872	101
102	61.18	.026841	1.639	.6101	254.2	158.9	413.1	.9043	1.1872	102
103	62.13	.026874	1.615	.6193	254.8	158.6	413.4	.9053	1.1872	103
104	63.10	.026908	1.591	.6285	255.4	158.3	413.7	.9063	1.1872	104

TABLE 2.—Properties of saturated 1, 3-butadiene—Continued

Temperature, <i>t</i>	Abs. pressure	Specific volume		Density vapor $1/v_g$	Enthalpy			Entropy		Temperature, <i>t</i>
		v_f	v_g		Liquid h_f	Evap. h_{fg}	Vapor h_g	Liquid s_f	Vapor s_g	
$^{\circ}F$	lb/in. ²	ft ³ /lb	ft ³ /lb	lb/ft ³	Btu/lb	Btu/lb	Btu/lb	Btu/lb [∘] R	Btu/lb [∘] R	$^{\circ}F$
105	64.07	0.026941	1.568	0.6379	256.0	158.0	414.0	0.9073	1.1872	105
106	65.06	.026975	1.545	.6474	256.4	157.8	414.2	.9083	1.1872	106
107	66.06	.027009	1.522	.6570	257.0	157.5	414.5	.9093	1.1872	107
108	67.07	.027043	1.500	.6668	257.6	157.2	414.8	.9103	1.1872	108
109	68.09	.027077	1.478	.6766	258.2	156.9	415.1	.9113	1.1872	109
110	69.12	.027112	1.457	.6865	258.8	156.6	415.4	.9123	1.1872	110
111	70.17	.027146	1.436	.6966	259.3	156.3	415.6	.9133	1.1872	111
112	71.23	.027181	1.415	.7068	259.9	156.0	415.9	.9143	1.1872	112
113	72.29	.027216	1.395	.7171	260.5	155.7	416.2	.9153	1.1872	113
114	73.37	.027251	1.375	.7275	261.1	155.4	416.5	.9163	1.1872	114
115	74.47	.027286	1.355	.7380	261.7	155.1	416.8	.9173	1.1872	115
116	75.57	.027322	1.336	.7487	262.2	154.8	417.0	.9183	1.1872	116
117	76.69	.027358	1.317	.7595	262.8	154.5	417.3	.9193	1.1872	117
118	77.82	.027393	1.298	.7704	263.4	154.2	417.6	.9203	1.1872	118
119	78.96	.027429	1.280	.7814	264.0	153.9	417.9	.9213	1.1873	119
120	80.11	.027466	1.262	.7926	264.6	153.6	418.2	.9223	1.1873	120
121	81.28	.027502	1.244	.8039	265.1	153.3	418.4	.9233	1.1873	121
122	82.46	.027538	1.227	.8153	265.7	153.0	418.7	.9243	1.1873	122
123	83.65	.027575	1.209	.8268	266.3	152.7	419.0	.9253	1.1873	123
124	84.85	.027612	1.193	.8385	267.0	152.3	419.3	.9263	1.1873	124
125	86.07	.027649	1.176	.8503	267.5	152.0	419.5	.9273	1.1873	125
126	87.30	.027687	1.160	.8623	268.1	151.7	419.8	.9283	1.1874	126
127	88.54	.027724	1.144	.8743	268.7	151.4	420.1	.9293	1.1874	127
128	89.80	.027762	1.128	.8865	269.3	151.1	420.4	.9303	1.1874	128
129	91.07	.027800	1.112	.8989	269.8	150.8	420.6	.9313	1.1874	129
130	92.35	.027838	1.097	.9114	270.4	150.5	420.9	.9323	1.1874	130
131	93.65	.027877	1.082	.9240	271.1	150.1	421.2	.9333	1.1875	131
132	94.96	.027915	1.067	.9368	271.7	149.8	421.5	.9343	1.1875	132
133	96.28	.027954	1.053	.9497	272.2	149.5	421.7	.9353	1.1875	133
134	97.62	.027993	1.039	.9628	272.8	149.2	422.0	.9363	1.1875	134
135	98.97	.028032	1.0246	.9760	273.5	148.8	422.3	.9373	1.1875	135
136	100.33	.028072	1.0108	.9893	274.0	148.5	422.5	.9383	1.1876	136
137	101.71	.028111	.9972	1.0028	274.6	148.2	422.8	.9392	1.1876	137
138	103.10	.028151	.9838	1.0165	275.2	147.9	423.1	.9402	1.1876	138
139	104.51	.028191	.9706	1.0303	275.9	147.5	423.4	.9412	1.1876	139
140	105.93	.028232	.9576	1.044	276.4	147.2	423.6	.9422	1.1877	140
141	107.36	.028272	.9449	1.058	277.0	146.9	423.9	.9432	1.1877	141
142	108.81	.028313	.9323	1.073	277.7	146.5	424.2	.9442	1.1877	142
143	110.27	.028354	.9199	1.087	278.2	146.2	424.4	.9452	1.1878	143
144	111.75	.028395	.9077	1.102	278.8	145.9	424.7	.9462	1.1878	144
145	113.24	.028437	.8957	1.116	279.5	145.5	425.0	.9472	1.1878	145
146	114.75	.028479	.8839	1.131	280.0	145.2	425.2	.9482	1.1878	146
147	116.27	.028521	.8723	1.146	280.7	144.8	425.5	.9492	1.1879	147
148	117.81	.028563	.8608	1.162	281.3	144.5	425.8	.9501	1.1879	148
149	119.36	.028606	.8496	1.177	281.9	144.1	426.0	.9511	1.1879	149
150	120.9	.028648	.8385	1.193	282.5	143.8	426.3	.9521	1.1880	150
151	122.5	.028691	.8275	1.208	283.1	143.5	426.6	.9531	1.1880	151
152	124.1	.028735	.8167	1.224	283.7	143.1	426.8	.9541	1.1880	152
153	125.7	.028778	.8061	1.240	284.4	142.7	427.1	.9551	1.1881	153
154	127.3	.028822	.7957	1.257	285.0	142.4	427.4	.9561	1.1881	154
155	129.0	.028866	.7854	1.273	285.6	142.0	427.6	.9571	1.1881	155
156	130.6	.028911	.7753	1.290	286.2	141.7	427.9	.9581	1.1882	156
157	132.3	.028956	.7653	1.307	286.8	141.3	428.1	.9590	1.1882	157
158	134.0	.029001	.7554	1.324	287.4	141.0	428.4	.9600	1.1883	158
159	135.7	.029046	.7458	1.341	288.0	140.6	428.6	.9610	1.1883	159

TABLE 2.—Properties of saturated 1, 3-butadiene—Continued

Temperature, <i>t</i>	Abs. pressure	Specific volume		Density vapor 1/ <i>v_g</i>	Enthalpy			Entropy		Temperature, <i>t</i>
		<i>v_f</i>	<i>v_g</i>		Liquid <i>h_f</i>	Evap. <i>h_{fg}</i>	Vapor <i>h_g</i>	Liquid <i>s_f</i>	Vapor <i>s_g</i>	
^o F	lb/in. ²	ft ³ /lb	ft ³ /lb	lb/ft ³	Btu/lb	Btu/lb	Btu/lb	Btu/lb ^o R	Btu/lb ^o R	^o F
160	137.4	0.029092	0.7362	1.358	288.6	140.3	428.9	0.9620	1.1883	160
161	139.2	.029138	.7268	1.376	289.3	139.9	429.2	.9630	1.1884	161
162	140.9	.029184	.7175	1.394	289.9	139.5	429.4	.9640	1.1884	162
163	142.7	.029230	.7084	1.412	290.5	139.2	429.7	.9650	1.1884	163
164	144.5	.029277	.6994	1.430	291.1	138.8	429.9	.9659	1.1885	164
165	146.3	0.29324	.6905	1.448	291.8	138.4	430.2	.9669	1.1885	165
166	148.1	.029372	.6818	1.467	292.3	138.1	430.4	.9679	1.1885	166
167	149.9	.029419	.6731	1.486	293.0	137.7	430.7	.9689	1.1886	167
168	151.8	.029467	.6646	1.505	293.7	137.3	431.0	.9699	1.1886	168
169	153.7	.029516	.6563	1.524	294.3	136.9	431.2	.9709	1.1887	169
170	155.5	.029565	.6480	1.543	294.9	136.5	431.4	.9719	1.1887	170
171	157.5	.029614	.6399	1.563	295.5	136.2	431.7	.9728	1.1887	171
172	159.4	.029663	.6318	1.583	296.2	135.8	432.0	.9738	1.1888	172
173	161.3	.029713	.6239	1.603	296.8	135.4	432.2	.9748	1.1888	173
174	163.3	.029763	.6161	1.623	297.4	135.0	432.4	.9758	1.1888	174
175	165.2	.029814	.6084	1.644	298.1	134.6	432.7	.9768	1.1889	175
176	167.2	.029865	.6008	1.664	298.8	134.2	433.0	.9778	1.1889	176
177	169.2	.029916	.5934	1.685	299.4	133.8	433.2	.9787	1.1890	177
178	171.3	.029968	.5860	1.707	300.0	133.4	433.4	.9797	1.1890	178
179	173.3	.030020	.5787	1.728	300.6	133.1	433.7	.9807	1.1890	179
180	175.4	.030072	.5715	1.750	301.3	132.6	433.9	.9817	1.1891	180
181	177.4	.030125	.5644	1.772	301.9	132.3	434.2	.9827	1.1891	181
182	179.5	.030178	.5575	1.794	302.5	131.9	434.4	.9837	1.1891	182
183	181.7	.030232	.5506	1.816	303.2	131.4	434.6	.9846	1.1892	183
184	183.8	.030286	.5438	1.839	303.9	131.0	434.9	.9856	1.1892	184
185	185.9	.030340	.5371	1.862	304.5	130.6	435.1	.9866	1.1892	185
186	188.1	.030395	.5305	1.885	305.2	130.2	435.4	.9876	1.1893	186
187	190.3	.030450	.5239	1.909	305.8	129.8	435.6	.9886	1.1893	187
188	192.5	.030506	.5175	1.932	306.4	129.4	435.8	.9896	1.1894	188
189	194.7	.030562	.5112	1.956	307.1	129.0	436.1	.9906	1.1894	189
190	197.0	.030619	.5049	1.981	307.7	128.6	436.3	.9915	1.1894	190
191	199.2	.030676	.4987	2.005	308.3	128.2	436.5	.9925	1.1895	191
192	201.5	.030734	.4926	2.030	309.1	127.7	436.8	.9935	1.1895	192
193	203.8	.030792	.4866	2.055	309.7	127.3	437.0	.9945	1.1895	193
194	206.1	.030850	.4806	2.081	310.3	126.9	437.2	.9955	1.1895	194
195	208.5	.030909	.4748	2.106	311.0	126.4	437.4	.9964	1.1896	195
196	210.9	.030969	.4690	2.132	311.7	126.0	437.7	.9974	1.1896	196
197	213.2	.031029	.4632	2.159	312.3	125.6	437.9	.9984	1.1896	197
198	215.6	.031090	.4576	2.185	313.0	125.1	438.1	.9994	1.1897	198
199	218.1	.031151	.4520	2.212	313.6	124.7	438.3	1.0004	1.1897	199
200	220.5	.031213	.4465	2.240	315	124	439	1.001	1.190	200
202	225.4	.031337	.4357	2.295	316	123	439	1.003	1.190	202
204	230.5	.031464	.4252	2.352	317	122	439	1.005	1.190	204
206	235.6	.031594	.4149	2.410	318	122	440	1.007	1.190	206
208	240.8	.031726	.4049	2.470	319	121	440	1.009	1.190	208
210	246.0	.031861	.3951	2.531	321	120	441	1.011	1.190	210
212	251.4	.031998	.3856	2.594	322	119	441	1.013	1.190	212
214	256.8	.032138	.3763	2.658	323	118	441	1.015	1.190	214
216	262.4	.032281	.3672	2.732	325	117	442	1.017	1.190	216
218	268.0	.032427	.3583	2.791	326	116	442	1.019	1.190	218
220	273.7	.032576	.3496	2.860	328	115	443	1.021	1.190	220
222	279.5	.032728	.3411	2.931	329	114	443	1.023	1.190	222
224	285.4	.032884	.3329	3.004	330	113	443	1.025	1.190	224
226	291.4	.033044	.3248	3.079	332	112	444	1.027	1.190	226
228	297.5	.033207	.3168	3.156	333	111	444	1.029	1.190	228

TABLE 2.—Properties of saturated 1, 3-butadiene—Continued

Temperature, <i>t</i>	Abs. pressure	Specific volume		Density vapor $1/v_g$	Enthalpy			Entropy		Temperature, <i>t</i>
		v_f	v_g		Liquid h_f	Evap. h_{fg}	Vapor h_g	Liquid s_f	Vapor s_g	
$^{\circ}F$	lb/in. ²	ft ³ /lb	ft ³ /lb	lb/ft ³	Btu/lb	Btu/lb	Btu/lb	Btu/lb [∘] R	Btu/lb [∘] R	$^{\circ}F$
230	303.7	0.03337	0.3091	3.235	334	110	444	1.031	1.190	230
232	310.0	.03354	.3015	3.317	336	109	445	1.033	1.190	232
234	316.3	.03372	.2941	3.400	338	107	445	1.035	1.190	234
236	322.8	.03390	.2868	3.487	339	106	445	1.037	1.190	236
238	329.4	.03408	.2797	3.575	341	105	446	1.039	1.190	238
240	336.1	.03427	.2727	3.667	342	104	446	1.041	1.190	240
242	342.9	.03447	.2659	3.761	343	103	446	1.043	1.190	242
244	349.8	.03467	.2592	3.858	344	102	446	1.045	1.189	244
246	356.8	.03488	.2526	3.959	347	100	447	1.047	1.189	246
248	363.9	.03509	.2462	4.062	348	99	447	1.049	1.189	248
250	371.1	.03531	.2398	4.170	349	98	447	1.051	1.189	250
252	378.5	.03554	.2336	4.281	351	96	447	1.053	1.189	252
254	385.9	.03578	.2274	4.397	352	95	447	1.055	1.189	254
256	393.5	.03603	.2214	4.517	354	94	448	1.057	1.188	256
258	401.2	.03628	.2155	4.640	356	92	448	1.059	1.188	258
260	409	.0365	.2097	4.770	357	91	448	1.062	1.188	260
262	417	.0368	.2039	4.904	359	89	448	1.064	1.187	262
264	425	.0371	.1982	5.045	360	88	448	1.066	1.187	264
266	433	.0374	.1926	5.192	362	86	448	1.068	1.187	266
268	441	.0377	.1870	5.347	364	84	448	1.070	1.186	268
270	450	.0381	.1815	5.51	365	83	448	1.073	1.186	270
272	459	.0384	.1761	5.68	367	81	448	1.075	1.185	272
274	467	.0388	.1707	5.86	369	79	448	1.077	1.185	274
276	476	.0392	.1653	6.05	370	77	447	1.079	1.184	276
278	485	.0396	.1599	6.25	372	75	447	1.082	1.183	278
280	494	.0401	.155	6.47	375	72	447	1.084	1.182	280
282	504	.0406	.149	6.71	376	70	446	1.087	1.181	282
284	513	.0411	.144	6.96	379	67	446	1.090	1.180	284
286	523	.0417	.138	7.24	380	65	445	1.092	1.179	286
288	533	.0424	.132	7.55	382	62	444	1.095	1.178	288

The values of enthalpy for the liquid have been given to hundredths of a Btu/lb where they were well supported by experimental data. In consequence of the rounding off of the values for the vapor and for evaporation, the latter may differ by one in the last place from the difference between the enthalpy of vapor and of liquid.

The values in the table and chart were calculated by methods described in a previous publication [8] after first converting the four empirical equations given in that publication to engineering units.

In computing the figures in the table from the empirical equations, all calculations were carried two digits beyond the number to be finally retained in the table. The values have been checked by differences.

The number of empirical equations used has been kept to a minimum, and exact thermodynamic relations have been used whenever possible.

In consequence, the values given in the table are thermodynamically consistent.

In consideration of the large size of tables for superheated vapor and of the fact that the data for 1,3-butadiene can be represented on a chart nearly within the accuracy of the observed data, the properties of the superheated vapor are presented only in graphical form.

VI. Description of the Mollier Chart

Five properties, namely, temperature, pressure, specific volume, enthalpy, and entropy are useful in solving thermodynamic problems. These properties may be presented either in a table or on a chart such as first designed by Mollier [9]. Any two of the properties may be plotted as coordinates, but enthalpy usually is chosen as one coordinate as it is the property for which numerical values are of most interest. Any one of the other

four properties or a function thereof may be used for the other coordinate, depending upon the nature of the problems to be solved and the individual preference of the user. In the present instance, the use of the logarithm of pressure gives a constant percentage accuracy in reading the pressure and utilizes the rectangular paper efficiently. Usually all five properties are included, but for the sake of clarity, the constant volume lines have been omitted from the present Mollier chart. Values for the volume may be derived from figures 3, 4, and 5.

The logarithms of pressures from 3 to 300 lb/in.² have been plotted as ordinates. Two scales along the abscissa have been used to represent enthalpies, the one at the left for the liquid, and the one at the right for the vapor. The curves representing the saturated vapor and the saturated liquid are so marked. The area to the left of the curve for saturated liquid represents the subcooled liquid for which no data are available. It should be noted that data for other substances indicate that the constant temperature lines are practically vertical over this area. The area between the curves for saturated liquid and for saturated vapor represents mixtures of vapor and liquid. It has not been charted and the distance between the two saturation lines has no physical significance. The area at the right represents superheated vapor up to 300° F.

The chart as originally drawn is 80 by 98 cm (approximately 31½ x 38½ in.). The mid points of each coordinate line were located by means of a beam compass and an accurate scale, and the coordinate lines drawn in by means of a parallel straight edge. Various checks indicate that the coordinates are drawn with an accuracy of 0.2 or 0.3 mm, corresponding to about 0.05 Btu/lb and to about two parts in 1,000 of the pressure.

Over 600 points were plotted so that each curve was drawn through a considerable number of suitably chosen points by means of a spline and weights. Errors in plotting larger than 0.2 or 0.3 mm became evident due to the difficulty of fitting the spline to the points with a reasonable number of weights. This estimate of the accuracy of plotting is supported by the fact that out of values read from 20 points on the original drawing, the largest discrepancy between the chart and calculated values was 0.05 Btu/lb (0.3

mm) and 0.0008 Btu/lb °R in entropy units (0.3 mm).

VII. Use of Tables and Charts

The usefulness of the table and Mollier chart is based largely on three properties of the thermodynamic function enthalpy (sometimes called heat content). The three properties referred to are (1) In any process that occurs at constant pressure the increase in enthalpy is equal to the heat added; (2) in adiabatic compression—that is, at constant entropy—the work done by the compressor is equal to the change in enthalpy of the fluid between intake and discharge; and (3) in a throttling process, such as occurs at an expansion valve, the increase in enthalpy is equal to the heat added. Therefore, when no heat is added the enthalpy is constant.

Two problems that illustrate the application of the three principles mentioned above, through use of the chart, will now be discussed.

Problem 1. Butadiene is admitted into a distillation unit as liquid under an absolute pressure of about 80 lb/in.² and at a temperature of 70° F. It is to be converted under the same pressure to gas at 120° F. How much heat must be added per pound of butadiene?

Due to lack of experimental data, the chart does not give values of enthalpy for the subcooled liquid; but from data on other substances it may be inferred that the change of enthalpy with pressure for subcooled liquid butadiene at constant temperature is so small that for all practical purposes the value at 80 lb/in.² absolute and 70° F is the same as the value 236.5 Btu/lb for saturated liquid at 70° F. The chart indicates that vapor leaving the still at 80 lb/in.² absolute pressure and 120° F is practically saturated vapor and that its enthalpy is 418.2 Btu/lb. The difference 418.2—236.5=181.7 Btu per lb must be supplied to the butadiene. The answer should be affected only slightly by the presence of appreciable amounts of other C₄ hydrocarbons, as they have properties very similar to butadiene, but the presence of dissimilar compounds renders the answer unreliable in such problems. The heat of solution is involved in evaporation of mixtures that for dissimilar substances may differ appreciably from the heat of evaporation for butadiene.

Although correct answers can be obtained only when these data are applied to the pure monomer

of 1,3-butadiene, yet in many of the problems to be solved, mixtures of the monomer with polymer or with other compounds are encountered. In some cases if the composition of the mixture is known, a judicious use of the chart may lead to a sufficiently approximate answer.

In the following problem, which involves such a mixture, the results of two methods of calculation with the use of the chart are compared with the results of a third method of calculation in which data are used from tables or charts appropriate for each component of the mixture.

The correct answer to this problem could be obtained only from measurements made on the mixture itself. Such data are rarely available, but the results obtained by the third method are believed to approach the correct answer most closely.

Problem 2. In some processes a gaseous mixture saturated with water vapor and containing about 90 percent of butadiene and 8 percent of ammonia is encountered. The initial temperature and pressure of this mixture will be assumed to be 78° F and 25 lb/in.², respectively. In actual practice the pressure of this mixture is increased only a few pounds per square inch through compression. We will assume for the present problem, however, a compression ratio of two, i. e. a discharge pressure of 50 lb/in.², for the sake of sizable differences on the Mollier chart that may be read with sufficient accuracy for the comparison of three methods of calculation. The problem will consist in finding (1) the work performed by the compressor (2) the temperature of the discharged gas and (3) the increase in work of compression caused by pressure drop through valves or other constrictions.

In the first method, the procedure is to calculate the results for pure butadiene as a rough approximation to the results for the mixture.

The initial condition is represented on the Mollier chart by the intersection between the pressure ordinate 25 lb/in.² and the constant temperature 78° F interpolated between the dotted curves for 70° F and for 80° F. This intersection corresponds to an enthalpy of 408.0 Btu/lb and an entropy of 1.209. The intersection of this value for entropy with the pressure ordinate 50 lb/in.² is at an enthalpy of 421.5 Btu/lb and a temperature of 120° F. Then for pure butadiene (1) the work of compression is 421.5—

408.0=13.5 Btu/lb and (2) the discharge temperature is 120° F.

A second method, which gives a better estimate of the work of compression, uses the chart by taking account of the fact that for equal compression ratios with the same inlet temperature, the work of compression per mole varies only 10 or 20 percent from substance to substance, whereas the work per unit mass varies over a wide range. On the molar basis the calculation is as follows:

$$\begin{aligned} 0.9 \text{ lb butadiene} &= 0.9/54 = 0.01665 \text{ lb mole.} \\ 0.08 \text{ lb ammonia} &= 0.08/17 = 0.00471 \text{ lb mole.} \\ 0.02 \text{ lb water} &= 0.02/18 = 0.00111 \text{ lb mole.} \end{aligned}$$

$$\text{Total} \text{-----} 0.02247 \text{ lb mole.}$$

$$1 \text{ lb butadiene} = 1/54 = 0.01852 \text{ mole.}$$

Work of compression for 1 lb of mixture is

$$13.5 \times 0.02247 / 0.01852 = 16.4 \text{ Btu/lb.}$$

The third and probably the best method for estimating the work of compression is to sum up the work for compressing the various components separately through the same compression ratio from their initial partial pressures. Fortunately, such procedure is possible for the mixture presented in this problem, as tables of the properties of ammonia [10] and of steam [11] are both available.

The partial pressures are for butadiene 22.5 lb/in.², for ammonia 2.0 lb/in.², and for water the saturation pressure at 78° F, which is given by Keenan and Keyes in their table 1 as 0.4747 lb/in.² Using the same procedure as before for butadiene at 25 lb/in.² initial pressure, and the same initial temperature 78° F and compression ratio, two, one finds the same values for the work and the discharge temperature, for example, 13.5 Btu/lb and 120° F, respectively.

The ammonia tables mentioned do not include pressures below 5 lb/in.² but the work of compression for a compression ratio of 2 and initial temperature 78° F is nearly independent of initial pressure. For initial pressures of 5 and 10 lb/in.², the work of compression is respectively 46.8 and 46.7 Btu/lb, the discharge temperature in both cases being 170.5° F. One may assume the work of compression to be 46.8 Btu/lb for an initial pressure of 2 lb/in.², and the discharge temperature 170° F.

The steam tables by Keenan and Keyes give

for the enthalpy and entropy of saturated steam at 78° F, respectively 1,095.8 Btu/lb and 2.0416 Btu/lb °R. The discharge pressure is $2 \times 0.4747 = 0.95$ lb/in.². For convenience we will use the rounded pressure 1 lb/in.². The enthalpy and temperature corresponding to an entropy of 2.0416 and a pressure of 1 lb/in.² are 1144.1 Btu/lb and 186° F, respectively. The work is then $1144.1 - 1095.8 = 48.3$ Btu/lb.

The work of compression for the mixture is then,

$$(0.9 \times 13.5) + (0.08 \times 46.8) + (0.02 \times 48.3) = 16.8 \text{ Btu/lb,}$$

and the discharge temperature is,

$$(0.9 \times (120 - 78)) + (0.08 \times (170 - 78)) + (0.02 \times (186 - 78)) + 78 = 125^\circ \text{ F.}$$

We now have three values calculated for the work of compression, namely:

- (1) For pure butadiene, 13.5 Btu/lb.
- (2) For the mixture, using the chart for butadiene together with the assumption that the work of compression per mole is the same for different substances, 16.4 Btu/lb.
- (3) For the mixture using the appropriate chart or table for each component of the mixture, 16.8 Btu/lb.

This last method would be expected to give the nearest to the correct answer, but cannot always be used as data may be lacking on some of the components.

The discharge temperature (120° F) for pure butadiene is in this case lower than that (125° F) for the mixture. This is due to the fact that the molar specific heats of ammonia and steam are less than that for butadiene.

The additional work that the compressor must perform in consequence of a pressure drop due to throttling through valves or other constrictions may be estimated by employing the third property previously mentioned for enthalpy, i. e. the constancy of enthalpy during a throttling process when no heat is added or removed. The loss is very nearly proportional to the pressure drop and may be calculated by multiplying the work per (lb/in.²) by the pressure drop. If on the Mollier chart we follow from the point representing intake conditions (78° F and 25 lb/in.²) downward along

the constant enthalpy abscissa (408.0 Btu/lb) to 24 lb/in.² the new entropy is 1.210. If this constant entropy line is followed back to 25 lb/in.² an enthalpy of (409.0 Btu/lb) is obtained. The additional work that the compressor must perform in consequence of a 1 lb/in.² pressure drop in the suction line is $409 - 408 = 1$ Btu/lb. By a similar process one finds that 1 lb/in.² pressure drop on the discharge side where the pressure is 50 lb/in.² causes the compressor to perform extra work amounting to 0.5 Btu/lb. In the case where the total compression amounts to only a few pounds, losses due to pressure drop may become an important portion of the whole.

VIII. Graphs of Certain Properties of 1, 3-Butadiene

A number of smaller graphs of the properties of butadiene are presented in this publication (1) to furnish data not readable directly from the Mollier chart and (2) to give the reader a clearer picture of the basis for, and relationships between these data. Figure 1 in which enthalpy (Btu/lb) is plotted vs temperature (°F) is especially in the latter class.

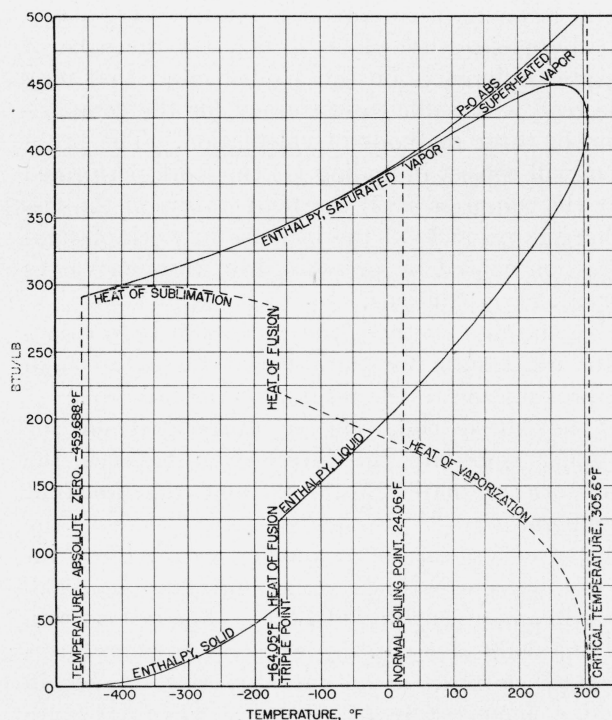


FIGURE 1.—Enthalpy of saturated 1, 3-butadiene.

As will be noted in this figure, the value for the enthalpy of the crystalline solid has been taken as zero. This has been done for two reasons, namely, (1) except in problems involving chemical reactions no negative numbers are encountered with such choice (2) as many of the theoretical calculations of thermodynamics are based on the theorem that the entropy of crystalline substances is zero at the absolute zero of temperature, the zero for entropy was chosen for this state, and it seemed appropriate to assume the same state for the zero of enthalpy.

This choice of zero state is satisfactory for all the problems for which this publication was designed. A value for the heat of formation from the elements [12] may be added to the enthalpies used here, but its assignment was considered beyond the scope of this publication. As illustrated by the continuous curve in the lower left hand corner of figure 1, the enthalpy for solid butadiene gradually increases with temperature up to the triple point (-164.05°F) then increases through fusion to liquid without any change in temperature. When the liquid is warmed, the enthalpy again changes with temperature at a rate that gradually increases. The normal boiling point is reached at 24.06°F , in other words the vapor pressure has increased to one standard atmosphere. With further warming of the liquid, the enthalpy continued to increase at a rate that becomes infinite at the critical temperature 305.6°F , although the enthalpy itself is finite (about 421 Btu/lb).

The heat of vaporization is zero at the critical temperature, but increases to finite values as the temperature is decreased (see dotted curve fig. 1). The rate of increase at the critical is infinite but finite at lower temperatures. At the triple point the heat of sublimation exceeds the heat of vaporization by an amount equal to the heat of fusion. At lower temperatures the heat of sublimation increases to a maximum and then decreases. As near as can be deduced from values of C_p° from this formulation [8] together with the assumption that C_p° for the vapor approaches asymptotically toward $4R$ at absolute zero, the enthalpy of the vapor and consequently the heat of sublimation at absolute zero is about 287 Btu/lb. The enthalpy of the saturated vapor is the sum of the enthalpy for the solid and heat of sublimation, or at higher temperatures the sum of the enthalpy for

the liquid and the heat of vaporization. The enthalpy of saturated vapor increases with temperature without any break at the triple point, passes through a maximum at about 265°F and joins up with the enthalpy of the liquid at the critical temperature. The enthalpy of the vapor at zero pressure, which is the same as that at the standard state (ideal gas at 1 atm), is not distinguishable from the enthalpy of the saturated vapor at low temperatures, but at higher temperatures the difference calculated from the equation of state increases so that the enthalpy at $p=0$ increases steadily with temperature without any peculiar turn at the critical temperature as exhibited for the saturated vapor.

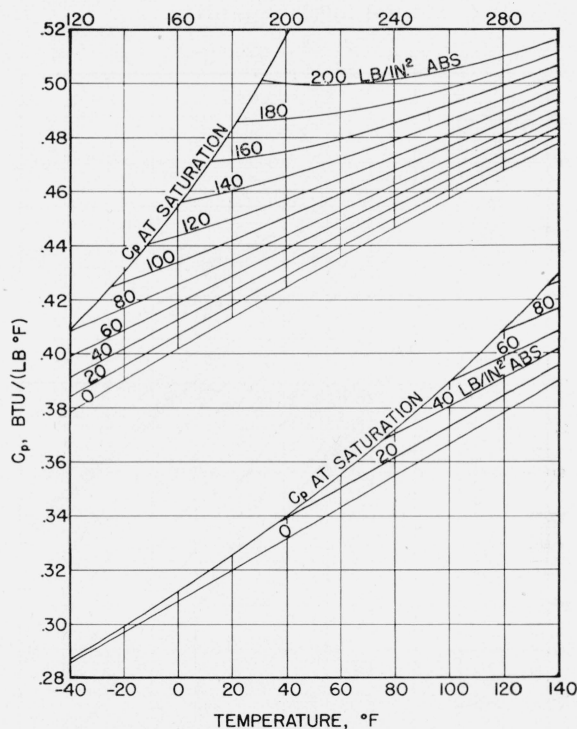


FIGURE 2.—Specific heat at constant pressure of gaseous 1, 3-butadiene.

Figure 2 is a plot of C_p the specific heat of the vapor at various pressures from 0 absolute to 200 lb/in.² abs as a function of temperature expressed in degrees F. The values of C_p at zero pressure are calculable from spectroscopic data but were actually calculated from an empirical equation [8] and the values at other pressures can be deduced from these by using the equation of state. The temperatures at the bottom of the graph apply to the lower set of curves, those at the

top to the upper set, with the two sets overlapping in the range 120° to 140° F. The curve for 200 lb/in.² shows a minimum in C_p for the vapor, and if the curves were computed for higher pressures, these minimums would be more pronounced.

Figure 3 shows values of the quantity Pv/RT (which is unity for an ideal gas) as a function of pressure for saturated vapor and for superheated vapor at various temperatures. It may be noted that at the highest pressure plotted, 120 lbs/in.² the value of Pv for saturated vapor is more than 16 percent less than the value for an ideal gas, but that at low pressure, the values of Pv approach RT , the approach being closer for the higher temperatures.

Figure 4 is a plot of the quantity $\frac{1-Pv/RT}{P(\text{lbs/in.}^2)} 10^4$

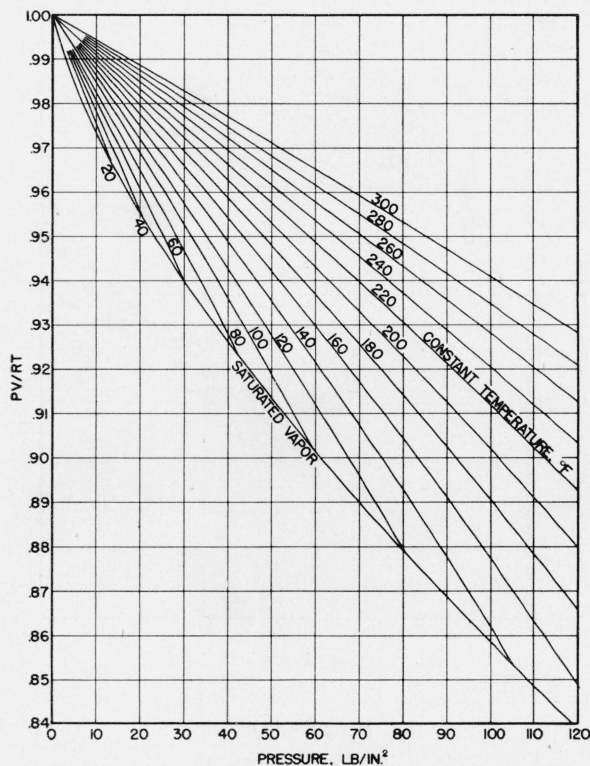


FIGURE 3.—Pressure-volume-temperature relations for gaseous 1, 3-butadiene.

(which is equal to zero for an ideal gas) for the vapor, as a function of the absolute pressure for various temperatures from -40° to 180° F. The quantity plotted never reaches the value for an ideal gas, but approaches it as the pressure is decreased or as the temperature is raised.

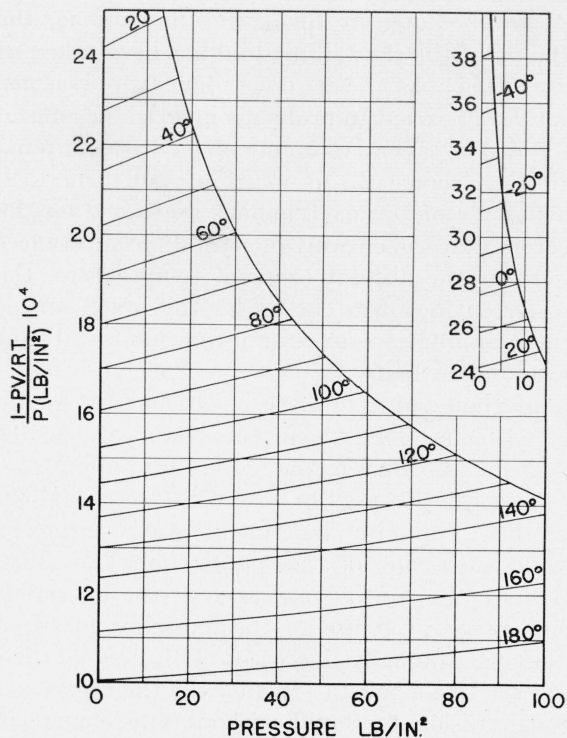


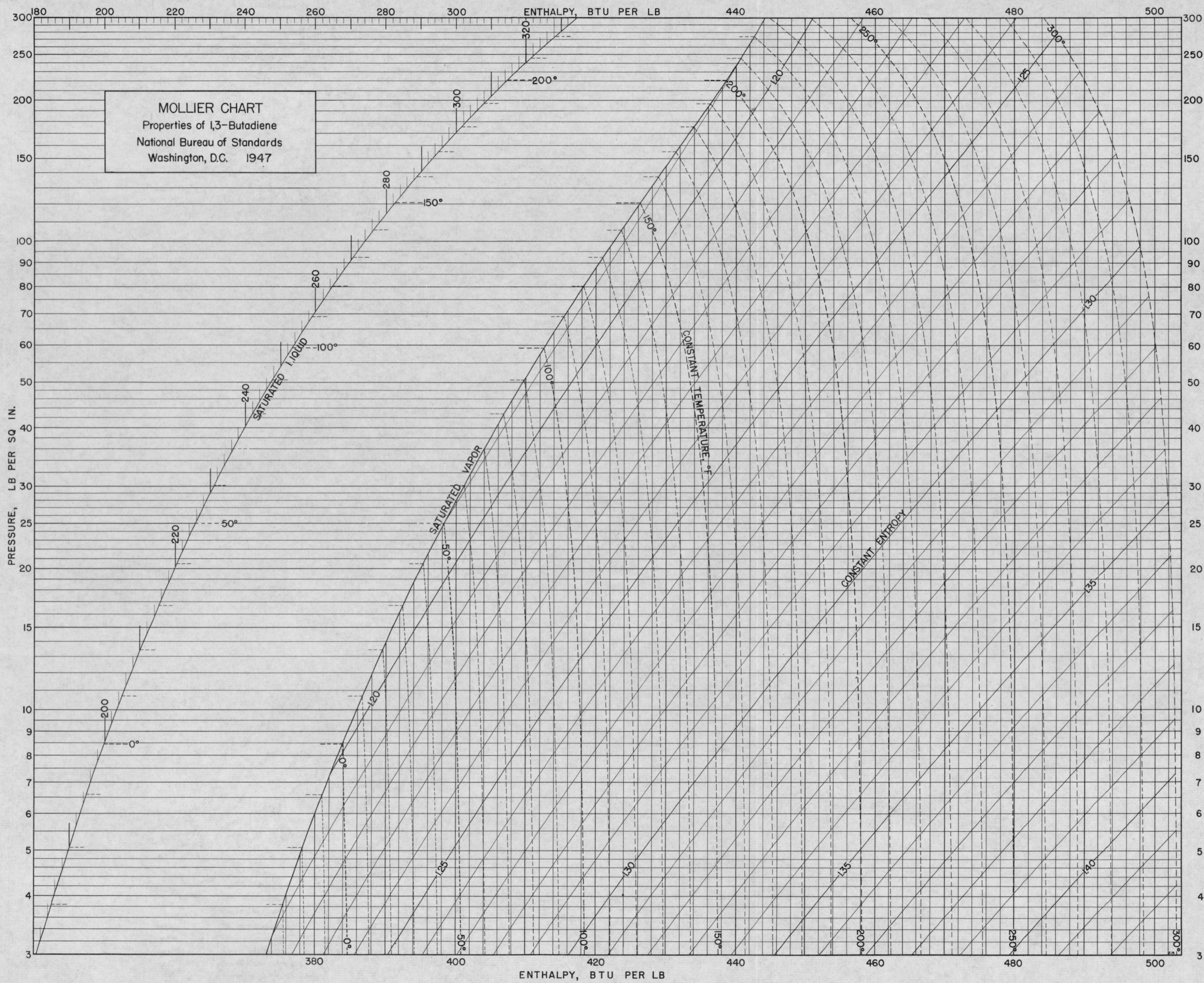
FIGURE 4.—Pressure-volume-temperature relations for gaseous 1, 3-butadiene.

For use at higher pressures and temperatures the coordinates used in figure 4 require too large a page for accurate presentation of the data. This difficulty is overcome in figure 5 by plotting

the product $\frac{1-Pv/RT}{P(\text{lb/in.}^2)} \left(\frac{T}{100}\right)^3$ as ordinate vs pres-

sure as abscissa. Through the use of these coordinates accurate values of Pv/RT may be obtained over the whole pressure and temperature range although more calculation is involved than in using figure 4. The isotherms cross each other as well as the saturation curve at low pressures and temperatures. In this region the isotherms have been omitted and the use of figure 4 will be less ambiguous.

An acknowledgment with thanks is given to Martin T. Wechsler for calculating the values appearing in the table and to Robert E. McCoskey for calculating the data needed for the Mollier chart and for drawing this chart.



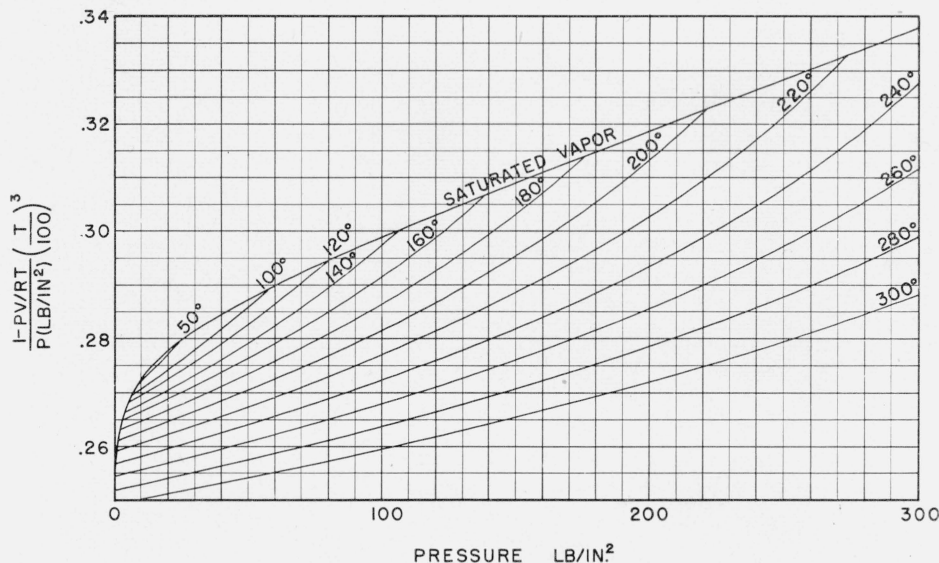


FIGURE 5.—Pressure-volume-temperature relations for gaseous 1, 3-butadiene.

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WASHINGTON, July 28, 1947.