R-8248

DIBORANE HANDBOOK

By

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FOREWORD

This propellant handbook is submitted as the final report under Rocketdyne G.O. 09239 in compliance with Contract NAS7-769, Article II, Paragraph D. The effort under this contract was sponsored by the National Aeronautics and Space Administration, Jet Propulsion Laboratory. The work was under the technical direction of Donald L. Young of the Jet Propulsion Laboratory, Pasadena, California and the NASA Headquarters Project Manager was Mr. Frank Stephenson.

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The following technical personnel contributed to compilation and analysis of the data and information contained in the handbook: Miss K. J. Youel, Mr. J. Q. Weber, Dr. M. Ladacki, Dr. L. R. Grant, Mr. W. H. Moberly, and Dr. V. H. Dayan.

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ABSTRACT

This handbook is a detailed compilation of the properties, handling procedures, and design criteria for diborane. Information on diborane physical and chemical properties, production, chemical analysis, storability, materials compatibility, materials preparation, facilities and equipment, disposal, transportation, and safety has been included. An extensive bibliography of diborane references is also included.

ACKNOWLEDGEMENTS

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SECTION 1: INTRODUCTION

1.1 GENERAL

1.1.1 Objective

The high potential performance and good physical characteristics of diborane (B_2H_6) make this compound an extremely attractive fuel for use with oxygen difluoride (OF_2) or FLOX (F_2-O_2 mixtures) in space-storable propulsion applications. Thus, there is a requirement for accurate and complete information and data on the physical, chemical, and engineering properties of this fuel. Although much of the required data and information already exists or is being generated under current research and development programs, very few of the data have been assembled and summarized in definitive manuals of engineering information.

The overall objective of this handbook is to provide a comprehensive and systematized assembly of existing data and information, relevant to the use of diborane in the propulsion industry, in a single, useable, and easily accessible text. Deficiencies in the presently available data are noted in this handbook and the presentation format is designed for incorporation of new and/or additional data as they are generated.

The data and information presented herein have been collected from government and industry reports, books, research papers, manufacturers' bulletins, patent literature, private communications, etc. All available information on physical and chemical properties, production, chemical analysis and specification, storage, materials compatibility, system and component design criteria, handling, transportation, safety, and other pertinent engineering data relevant to the application of diborane in the propulsion industry have been included. The total information has been reviewed, critically evaluated, correlated, and compiled, and arranged in an easy to use format.

1.1.2 Historical Development of Diborane

The emergence of diborane as a primary candidate for propulsion system applications has been a lengthy evolution. From its early study as a laboratory curiosity, through its growth as the precursor for the entire borane family of energetic fuels, the assembly of the diborane technology has been the product of a very large number of individuals and organizations working under a variety of objectives. The nature of this technology growth is discussed briefly in the following paragraphs.

The boron hydrides or boranes, of which diborane is the parent member, have been known to exist since the time of Sir Humphrey Davy, but not until the development of the vacuum technique by Alfred Stock in the early 1900's were they isolated and characterized (Ref. 1.1). The first synthesis of diborane by Stock in 1912 (Ref. 1.2) involved several months of effort to obtain even a few grams of the product. The second, less tedious, process was introduced by Schlesinger and Burg in 1931 and made possible the preparation of B_2H_6 at the rate of several tenths of a gram per day (Ref. 1.3). The World War II effort altered the situation, however, and new synthetic methods were sought (Ref. 1.4).

During the closing years of World War II, a need for a more energetic aircraft fuel was recognized. Military operations were requiring greater efficiencies from their airborne weapons in terms of greater distance and larger payloads. By 1946, this requirement had been translated into detailed studies (Project Hermes) of the use of the boranes as fuels for air-breathing engines. In 1952, the United States Department of Defense initiated Project ZIP; the objective of this large program was to develop high-energy, low-molecular weight compounds with high heats of combustion and physical properties similar to conventional hydrocarbon aircraft fuels (boranes were the compounds of choice). Consequently, scientists from universities, industry, and government pursued broad research programs in the field of boron chemistry, particularly in the development of practicable syntheses of boron hydrides and their derivatives.

Since diborane is the precursor of nearly all of the higher boron hydrides, its synthesis and attendant characterization received much attention; however, the primary emphasis of these earlier studies was on the development of alkylated derivatives of the boranes, i.e., propylpentaborane (HEF-2) and the ethyldecaboranes (HEF-3, HiCal-2, and HiCal-3). These fuels were prepared by alkylation of diborane with subsequent pyrolysis, or the pyrolysis of diborane to pentaborane (B_5H_9) and decaborane ($B_{10}H_{14}$) with subsequent alkylation of these products (Ref. 1.5, 1.6, and 1.7).

In the early 1960's, studies were directed at establishment of the boranes as rocket fuels. Although these studies were primarily concerned with the development, characterization, and evaluation of pentaborane for earth-storable propulsion applications, some consideration was also given to the potential rocket propulsion applications of the alkylated boranes and decaborane (both as a solid and as an ingredient in liquid mixtures). By the middle 1960's, interest in the higher boranes as rocket propellants had waned, but NASA advanced space system requirements resulted in a continued interest in diborane. As a result of this interest, current studies are being conducted to continue the growth of the diborane technology and develop it as a primary fuel for space-storable propulsion applications.

1.2 HANDBOOK FORMAT

The information in this handbook has been organized into seven sections:

Section 1: Introduction
Section 2: Physico-Chemical Properties
Section 3: Production and Chemical Analysis
Section 4: Storage and Handling
Section 5: Transportation
Section 6: Safety
Section 7: Bibliography

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Each of these sections has been subdivided further into more specific subject areas, and the material is arranged to permit convenient updating of these subject areas as additional data are generated.

The interest of each individual user may be limited to specific aspects of the material; however, it is recommended that personnel involved in diborane handling be thoroughly familiar with all of the engineering properties contained in this report. Although every effort has been made to provide presently available information on diborane in sufficient detail for most of the users of the handbook, size limitations of the handbook preclude inclusion of every conceivable detail. Thus, for those users who desire additional details on specific items related to diborane, consultation of the many referenced publications and the included bibliography is recommended.

The data and information referenced are from final reports whenever possible. In those efforts where a final report has not been issued or does not contain sufficient detail of the item, the data were taken from the latest progress report containing pertinent results.

The tables, figures, and references noted in each section are contained in the latter part of that particular section. For convenience, each table, figure, and reference number is preceded by the section number (i.e., Table 1.3 is the third table in Section 1, etc.).

Because the major portion of this handbook is related to areas of engineering interests, a major portion of the data, except that contained in Section 2.3, is presented in Engineering terminology (i.e., English units). The data in Section 2.3 are presented in the terminology (i.e., metric units) of the primary users of these sections. However, as a convenience to all of the users, data in certain sections (notably, the Physical Properties section) of the handbook are presented in both metric and English units. Where data are presented in both units, the unbracketed data in the attendant discussion indicate the units of the original work.

The assembly of the handbook has been designed for loose-leaf binding so that pages can be added, replaced, and/or removed as new or revised data on diborane become available. In this design, blank pages have been provided at various and convenient intervals to accommodate future additions to the manual with minimum revision of the existing pages. These blank pages can also provide convenient places for the insertion of notes by the user.

1.3 PHYSICAL CONSTANTS AND CONVERSION FACTORS

As a further convenience to the user, physical constants and conversion factors are presented in Sections 1.3.1 through 1.3.3. These constants and conversion factors are presented to the known degree of significance, but can be rounded to fit particular requirements.

1.3.1 Physical Constants

The following set of physical constants has been taken from a compilation by Rossini, F. D. et al., American Petroleum Institute Research Project 44, U.S. Department of Commerce, Natl. Bur. Standards, Circular 461, U.S. Government Printing Office, Washington, D.C. 1947 as revised by Rossini, F. D., J. Pure, Appl Chem., 8, 95 (1964).

Symbol	Constant	Value
g_c	Standard gravitational acceleration	32.1740 ft/sec^2 980.665 cm/sec^2
atm	Standard atmosphere	1,013,250 dynes/sq cm
mm Hg	Standard millimeter Hg	1333.2237 dynes/sq cm
cal	Thermochemical calorie	4.1840 abs joules 41.2929 ±0.0020 cu cm-atm
cal (I.T.)	International Steam Tables calorie	1.000654 thermochemical calories
T_0 C	Ice Point	491.67 ±0.018 R 273.15 ±0.010 K
$(PV)_{0\ C}^{P=0} = (RT)_{0\ C}$	Pressure-Volume product for ideal gas at 0 C	22,414.6 ±0.4 cu cm-atm/g mole 2271.16 ±0.04 abs joules/g mole
R	Molar gas constant	8.31439 ±0.00034 abs joules/K-g mole 1.98719 ±0.00013 cal/K-g mole 82.0567 ±0.0034 cu cm-atm/K-g mole 59.47 cu ft-atm/R-lb mole 10.73 cu ft-psia/R-lb mole
Btu	British thermal unit	1055.040 abs joules 252.161 thermochemical calories 251.996 I.T. calories
in.	United States unit	2.54000508 cm
ft	United States unit	30.4800610 cm
lb	Avoirdupois	453.5924277 g
gal	United States unit	0.133680555 cu ft 3785.43449 cu cm

1.3.2 Conversion Factors

The following conversion factors are calculated from the physical constants of Section 1.3.1 and are the values used for the conversions in this handbook.

Multiply	By	To Obtain
Temperature		
C	1.8	F -32
C + 273.15	1	K
K	1.8	R
F + 32	0.5555^+	C
R	0.5555^+	K
F + 459.67	1	R
Pressure		
atm	14.6960	psia
mm Hg	1.315790×10^{-3}	atm
mm Hg	0.0193368	psia
dyne/sq cm	1.450377×10^{-5}	psia
psig + 14.6960	1	psia
Length		
cm	0.3937008	inch
cm	0.0328084	feet
Area		
sq cm	0.1550003	sq in.
sq cm	1.076391×10^{-3}	sq ft
sq ft	144	sq in.
Volume		
cu cm	0.061023744	cu in.
cu cm	3.5314667×10^{-5}	cu ft
cu in. (U.S.)	5.787037×10^{-4}	cu ft
Force		
dynes	1.019716×10^{-3}	grams (force)
dynes	2.248089×10^{-6}	pounds (weight)
Energy		
cal*	3.9683207×10^{-3}	Btu
cal*	4.18400	joule
joule (abs)	9.48451×10^{-4}	Btu
Density & Specific Volume		
g/cc	62.427961	lb/cu ft
g/cc	8.3454044	lb/gal (U.S., liq)
cc/g	0.01601846	cu ft/lb

*This is the calorie as defined by the U.S. National Bureau of Standards

Multiply	By	To Obtain
Compressibility & Coefficient of Thermal Expansion		
sq cm/dyne	1.01325 x 10^{-6}	atm^{-1}
sq cm/dyne	6.8947 x 10^{-4}	$psia^{-1}$
$psia^{-1}$	14.696	atm^{-1}
C^{-1}	0.5555^{+}	F^{-1}
Surface Tension		
dynes/cm	6.852177 x 10^{-5}	lbf/ft
dynes/cm	5.710146 x 10^{-6}	lbf/in.
Energy Content		
cal/g	1.8	Btu/lb
cal/g-mole	1.8	Btu/lb-mole
cal/g-mole-K	1	Btu/lb-mole-R
joules/g	0.429922	Btu/lb
joules/g-K	0.239006	Btu/lb-R
cal/g	mol. wt.	cal/g-mole
Btu/lb	mol. wt.	Btu/lb-mole
Viscosity		
poise (g/cm-sec)	0.0672	lbm/ft-sec
centipoise	6.72 x 10^{-4}	lbm/ft-sec
centistokes	density (g/cc)	centipoise
Thermal Conductivity		
cal/cm-sec-K	241.9088	Btu/ft-hr-F
milliwatt/cm-sec-K	1.604970 x 10^{-5}	Btu/ft-sec-R
Velocity of Sound		
m/sec	3.28084	ft/sec

1.3.3 Temperature Conversion

Temperature Range																				
-459 to 0			0 to 50			50 to 100			100 to 490			500 to 1000			1000 to 1490			1500 to 2000		
C	T	F	C	T	F	C	T	F	C	T	F	C	T	F	C	T	F	C	T	F
-273	-459		-17.8	0	32.0	10.0	50	122.0	38	100	212	260	500	932	538	1000	1832	816	1500	2732
-268	-450		-17.2	1	33.8	10.6	51	123.8	43	110	230	266	510	950	543	1010	1850	821	1510	2750
-262	-440		-16.7	2	35.6	11.1	52	125.6	49	120	248	271	520	968	549	1020	1868	827	1520	2768
-257	-430		-16.1	3	37.4	11.7	53	127.4	54	130	266	277	530	986	554	1030	1886	832	1530	2786
-251	-420		-15.6	4	39.2	12.2	54	129.2	60	140	284	282	540	1004	560	1040	1904	838	1540	2804
-246	-410		-15.0	5	41.0	12.8	55	131.0	66	150	302	288	550	1022	566	1050	1922	843	1550	2822
-240	-400		-14.4	6	42.8	13.3	56	132.8	71	160	320	293	560	1040	571	1060	1940	849	1560	2840
-234	-390		-13.9	7	44.6	13.9	57	134.6	77	170	338	299	570	1058	577	1070	1958	854	1570	2858
-229	-380		-13.3	8	46.4	14.4	58	136.4	82	180	356	304	580	1076	582	1080	1976	860	1580	2876
-223	-370		-12.8	9	48.2	15.0	59	138.2	88	190	374	310	590	1094	588	1090	1994	866	1590	2894
-218	-360		-12.2	10	50.0	15.6	60	140.0	93	200	392	316	600	1112	593	1100	2012	871	1600	2912
-212	-350		-11.7	11	51.8	16.1	61	141.8	99	210	410	321	610	1130	599	1110	2030	877	1610	2930
-207	-340		-11.1	12	53.6	16.7	62	143.6	100	212	414	327	620	1148	604	1120	2048	882	1620	2948
-201	-330		-10.6	13	55.4	17.2	63	145.4	104	220	428	332	630	1166	610	1130	2066	888	1630	2966
-196	-320		-10.0	14	57.2	17.8	64	147.2	110	230	446	338	640	1184	616	1140	2084	893	1640	2984
-190	-310		- 9.44	15	59.0	18.3	65	149.0	116	240	464	343	650	1202	621	1150	2102	899	1650	3002
-184	-300		- 8.89	16	60.8	18.9	66	150.8	121	250	482	349	660	1220	627	1160	2120	904	1660	3020
-179	-290		- 8.33	17	62.6	19.4	67	152.6	127	260	500	354	670	1238	632	1170	2138	910	1670	3038
-173	-280		- 7.78	18	64.4	20.0	68	154.4	132	270	518	360	680	1256	638	1180	2156	916	1680	3056
-169	-273	-459	- 7.22	19	66.2	20.6	69	156.2	138	280	536	366	690	1274	643	1190	2174	921	1690	3074
-168	-270	-454	- 6.67	20	68.0	21.1	70	158.0	143	290	554	371	700	1292	649	1200	2192	927	1700	3092
-162	-260	-436	- 6.11	21	69.8	21.7	71	159.8	149	300	572	377	710	1310	654	1210	2210	932	1710	3110
-157	-250	-418	- 5.56	22	71.6	22.2	72	161.6	154	310	590	382	720	1328	660	1220	2228	938	1720	3128
-151	-240	-400	- 5.00	23	73.4	22.8	73	163.4	160	320	608	388	730	1346	666	1230	2246	943	1730	3146
-146	-230	-382	- 4.44	24	75.2	23.3	74	165.2	166	330	626	393	740	1364	671	1240	2264	949	1740	3164
-140	-220	-364	- 3.89	25	77.0	23.9	75	167.0	171	340	644	399	750	1382	677	1250	2282	954	1750	3182
-134	-210	-346	- 3.33	26	78.8	24.4	76	168.8	177	350	662	404	760	1400	682	1260	2300	960	1760	3200
-129	-200	-328	- 2.78	27	80.6	25.0	77	170.6	182	360	680	410	770	1418	688	1270	2318	966	1770	3218
-123	-190	-310	- 2.22	28	82.4	25.6	78	172.4	188	370	698	416	780	1436	693	1280	2336	971	1780	3236
-118	-180	-292	- 1.67	29	84.2	26.1	79	174.2	193	380	716	421	790	1454	699	1290	2354	977	1790	3254
-112	-170	-274	- 1.11	30	86.0	26.7	80	176.0	199	390	734	427	800	1472	704	1300	2372	982	1800	3272
-107	-160	-256	- 0.56	31	87.8	27.2	81	177.8	204	400	752	432	810	1490	710	1310	2390	988	1810	3290
-101	-150	-238	0	32	89.6	27.8	82	179.6	210	410	770	438	820	1508	716	1320	2408	993	1820	3308
- 95.6	-140	-220	0.56	33	91.4	28.3	83	181.4	216	420	788	443	830	1526	721	1330	2426	999	1830	3326
- 90.0	-130	-202	1.11	34	93.2	28.9	84	183.2	221	430	806	449	840	1544	727	1340	2444	1004	1840	3344
- 84.4	-120	-184	1.67	35	95.0	29.4	85	185.0	227	440	824	454	850	1562	732	1350	2462	1010	1850	3362
- 78.9	-110	-166	2.22	36	96.8	30.0	86	186.8	232	450	842	460	860	1580	738	1360	2480	1016	1860	3380
- 73.3	-100	-148	2.78	37	98.6	30.6	87	188.6	238	460	860	466	870	1598	743	1370	2498	1021	1870	3398
- 67.8	- 90	-130	3.33	38	100.4	31.1	88	190.4	243	470	878	471	880	1616	749	1380	2516	1027	1880	3416
- 62.2	- 80	-112	3.89	39	102.2	31.7	89	192.2	249	480	896	477	890	1634	754	1390	2534	1032	1890	3434
- 56.7	- 70	- 94	4.44	40	104.0	32.2	90	194.0	254	490	914	482	900	1652	760	1400	2552	1038	1900	3452
- 51.1	- 60	- 76	5.00	41	105.8	32.8	91	195.8				488	910	1670	766	1410	2570	1043	1910	3470
- 45.6	- 50	- 58	5.56	42	107.6	33.3	92	197.6				493	920	1688	771	1420	2588	1049	1920	3488
- 40.0	- 40	- 40	6.11	43	109.4	33.9	93	199.4				499	930	1706	777	1430	2606	1054	1930	3506
- 34.4	- 30	- 22	6.67	44	111.2	34.4	94	201.2				504	940	1724	782	1440	2624	1060	1940	3524
- 28.9	- 20	- 4	7.22	45	113.0	35.0	95	203.0				510	950	1742	788	1450	2642	1066	1950	3542
- 23.3	- 10	14	7.78	46	114.8	35.6	96	204.8				516	960	1760	793	1460	2660	1071	1960	3560
- 17.8	0	32	8.33	47	116.6	36.1	97	206.6				521	970	1778	799	1470	2678	1077	1970	3578
			8.89	48	118.4	36.7	98	208.4				527	980	1796	804	1480	2696	1082	1980	3596
			9.44	49	120.2	37.2	99	210.2				532	990	1814	810	1490	2714	1088	1990	3614
			10.00	50	122.0	37.8	100	212.0				538	1000	1832				1093	2000	3632

Interpolation Factors

C	T	F
0.56	1	1.8
1.11	2	3.6
1.67	3	5.4
2.22	4	7.2
2.78	5	9.0
3.33	6	10.8
3.89	7	12.6
4.44	8	14.4
5.00	9	16.2
5.56	10	18.0

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SECTION 2: PHYSICO-CHEMICAL PROPERTIES

2.1 GENERAL DESCRIPTION

Diborane is a boron hydride compound having the empirical formula B_2H_6. It is a colorless gas at room temperature with a critical temperature of 16.7 C (62.1 F) or 289.9 K (521.8 R). It is also colorless (water-white) in the solid and liquid states. Its odor has been variously described as unpleasant, distinctive, suggestive of new-mown hay, "like rotten eggs", and sweet. It is insensitive to mechanical shock but is very toxic. At room temperature, B_2H_6 decomposes slowly to hydrogen and higher-molecular-weight boron hydrides.

One of the most important properties of B_2H_6 is its high chemical reactivity. It is extremely flammable and usually ignites spontaneously in air; it is completely hydrolyzed by water. It reacts readily with halogens, reactive metals, various inorganic compounds, and many organic chemicals. However, it is this chemical reactivity that makes B_2H_6 an attractive rocket propellant.

Although B_2H_6 is very reactive and highly toxic, it will not present a serious storage or handling problem when stored and/or transferred at suitable temperature levels in clean, dry, compatible systems by properly trained personnel.

2.2 PHYSICAL PROPERTIES

Physical properties of B_2H_6, which have been previously determined in experimental and/or analytical investigations, have been evaluated and compiled. Nominal values for various phase, thermodynamic, transport, and electromagnetic properties, which are recommended as the most representative of the existing data, are summarized in Table 2.1.

All of the data presented are direct experimental determinations or are derived from curve-fits of the experimental data, except for those data referenced with an asterisk; the asterisked data represent calculations made during the referenced work which are based on standard analytical correlations and physical relationships.

Diborane properties for which property-temperature relationships have been established are presented in Table 2.1 at a designated temperature with a cross-reference figure number and/or table number, and reference number. The values given for these properties in Table 2.1 were established from their respective property-temperature plots (Fig. 2.1 through 2.11), which represent the curve-fits of the best experimental data. Equations representing the curve-fits over the noted temperature ranges are also included; the numbers of significant figures in these equations reflect the accuracy of the data.

A brief discussion of the available physical properties data for B_2H_6 is presented in the following paragraphs.

2.2.1 General Identification

The physical classifications under general identification are those properties that are used to identify B_2H_6 and its physical state.

2.2.1.1 Molecular Weight. The molecular weight of B_2H_6 was experimentally determined by vapor density measurements (Ref. 2.1). The resulting experimental value of 28.17 compares favorably to the value of 27.668 calculated from the International Atomic Weights (Ref. 2.2) according to the molecular formula.

2.2.1.2 Freezing (Melting) Point. The melting point of B_2H_6 has been experimentally determined by three different investigators (Ref. 2.3 through 2.5). The recommended value of 108.30 K (194.94 R, -164.85 C, or

-264.73 F) was reported in both Ref. 2.3 and 2.4 for samples with a purity greater than 99.9 mole percent, while a slightly lower value of -165.5 C (-265.9 F) was reported in the much older work of Ref. 2.5. In addition, the investigators of Ref. 2.4 also report a sharp melting point at 108.14 K (194.65 R, -165.01 C, or -265.02 F), which indicates that B_2H_6 can exist in two solid phases. However, no indications of phase transitions in the solid B_2H_6 were observed.

2.2.1.3 Triple Point. Although the triple point of B_2H_6 has not been explicitly defined (in terms of solid-liquid-vapor-equilibrium temperature, pressure, and volume), melting point measurements (Ref. 2.3 through 2.5) were conducted at saturated pressures. Thus the reported melting point is actually the triple point temperature.

2.2.1.3 Normal Boiling Point. A "normal boiling point" (equilibrium vapor pressure of 1 atmosphere or 14.7 psia) of 180.6 K (325.0 R, -92.6 C, or -134.7 F) was calculated for B_2H_6 from the curve-fit equations representing vapor pressure measurements on B_2H_6. This value is essentially in agreement with the normal boiling points calculated from the individual sets of vapor pressure measurements reported in Ref. 2.3, 2.4, and 2.6 through 2.8.

2.2.1.4 Critical Properties. The critical temperature and pressure of B_2H_6 were experimentally determined (Ref. 2.9) to be 16.7 C (289.9 K, 521.8 R, or 62.1 F) and 581 ±5 psia (39.5 ±0.3 atmospheres). A critical volume of 170 cc/mole (6.144 cc/g or 0.0984 cu ft/lb) was calculated (Ref. 2.6) as a part of the evaluation of liquid heat capacity data; from this value, a critical density of 0.163 g/cc (10.2 lb/cu ft) can be calculated. Using the equation of state for B_2H_6 discussed in Section 2.2.2.5, a critical density of 0.1658 g/cc (10.35 lb/cu ft) can be calculated. Since there is some question as to the overall accuracy of the equation of state, the value reported in Ref. 2.6 was arbitrarily selected.

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2.2.2 Phase Properties

Those properties of B_2H_6 which are associated with one particular phase (either solid, liquid, or gas) have been grouped as phase properties.

2.2.2.1 Density. The density of solid B_2H_6 was determined (Ref. 2.10) to be 0.577 g/cc (36.02 lb/cu ft) at -183 C (90 K, 162 R, or -298 F).

The density of saturated liquid B_2H_6 has been measured (Ref. 2.11 through 2.13) over the temperature range -129.5 C (-201.1 F) to the critical point. These data were curve-fitted from 143.7 to 285.2 K (258.7 to 513.4 R) to give the following equations which are shown graphically in Fig. 2.1 and 2.1a.

$$\rho_{(g/cc)} = 0.4857 + 7.618 \times 10^{-4} T_{(K)} - 5.747 \times 10^{-6} T^2_{(K)}$$

and

$$\rho_{(lb/cu\ ft)} = 30.32 + 2.642 \times 10^{-2} T_{(R)} - 1.107 \times 10^{-4} T^2_{(R)}$$

The standard errors of estimate for these equations are 0.0034 g/cc and 0.21 lb/cu ft, respectively.

It should be noted that no saturated liquid density data in the approximate temperature range of 181 to 235 K (326 to 423 R) were included in the least-squares analysis. Although some data for the saturated liquid have been reported (Ref. 2.14) in the range of 180.6 to 278.0 K (325.1 to 500.4 R), these data were obtained from an extrapolation of P-V-T data, experimentally determined at higher pressures, to the saturation temperatures. These extrapolated data are in disagreement with the individual experimental data at saturation (for corresponding temperatures), i.e., at the lower temperature end, these extrapolated data are lower, while at the higher temperatures they are higher. Also, the slope of a curve drawn through the extrapolated saturated liquid data of Ref. 2.14 is in disagreement with a consensus curve through the other sets of data.

The curve-fit correlation for the saturated liquid density covers nearly the entire temperature range of the measurements, but a few points near the critical point were omitted so that a simple polynomial equation could be used (a more complicated function would exhibit unacceptable behavior over the region with no data). In Fig. 2.1 and 2.1a, the correlated curve-fit has been extended through these additional experimental data to the critical point by means of a dashed line.

Density measurements on saturated B_2H_6 vapor have been reported in Ref. 2.11 and 2.14a; however, the two sets of data are not in good agreement. Although the data of Ref. 2.11 are reported to be accurate within ±3 percent, the scatter is actually much greater. The accuracy of these data has also been questioned (Ref. 2.15) on the basis of a comparison with values obtained from generalized P-V-T relations. Because a reasonable correlation could not be obtained using both sets of data, only the more recent work of Ref. 2.14a was used. These data were curve-fitted over the range 180.6 to 285.0 K (325.1 to 513.0 R, -92.6 to 11.8 C, or -134.8 to 53.3 F) to yield the following equations, which are presented graphically in Fig. 2.1b and 2.1c:

$$\log \rho_{(g/cc)} = 10.6409 - \frac{6528.72}{T_{(K)}} + \frac{1.19681 \times 10^6}{T_{(K)}^{2}} -$$

$$\frac{8.18767 \times 10^7}{T_{(K)}^{3}}$$

and

$$\log \rho_{(\mathrm{lb/cu\ ft})} = 12.4358 - \frac{11751.2}{T_{(R)}} + \frac{3.87745 \times 10^6}{T_{(R)}^{\ 2}} - \frac{4.77477 \times 10^8}{T_{(R)}^{\ 3}}$$

the standard error of estimate for these equations is 2.8 percent in density.

The composite representation of data for the saturated liquid and the saturated vapor, extrapolated through the calculated critical point, is presented in metric units in Fig. 2.1d.

2.2.2.2 Coefficient of Thermal Expansion. Cubical coefficients of thermal expansion were calculated for liquid B_2H_6 from the density data measured in Ref. 2.14 (see Section 2.2.2.1). These values, which cover a temperature range of 180.63 to 273.15 K (325.13 to 491.67 R, -92.53 to 0 C, or -134.56 to 32.00 F) and a pressure range of 10 to 60 atm (147 to 882 psia), are presented in Table 2.2.

2.2.2.3 Coefficient of Compressibility. There are no adiabatic compressibility data for liquid B_2H_6.

The isothermal compressibilities of liquid B_2H_6 were determined in Ref. 2.11 and 2.14 from P-V-T measurements. These two sets of data are in sharp disagreement, and there appears to be no way to ascertain which is the better set. Because the discrepancies are too large to obtain any reasonable correlation, the data of both investigators are simply reproduced in Tables 2.3 and 2.3a, respectively.

2.2.2.4 Vapor Pressure. The vapor pressure of liquid B_2H_6 has been experimentally determined by several investigators over the entire liquid range, and all of the data are in good agreement. The most recent (and also highest quality) data (Ref. 2.3, 2.4, and 2.6 through 2.8) were correlated with least-squares curve-fit equations from the melting point to the critical point. These equations, which are represented in Fig. 2.2 and 2.2a, are:

$$\log P_{(atm)} = 3.9426 - \frac{642.99}{T_{(K)} - 17.5}$$

and

$$\log P_{(psia)} = 5.1104 - \frac{1157.74}{T_{(R)} - 31.4}$$

The standard error of estimate for each of these equations is equivalent to 2.2 percent in P.

2.2.2.5 P-V-T Properties. A correlation of the P-V-T properties of B_2H_6 has been reported (Ref. 2.16) for the superheated vapor over the temperature range 130 to 1500 K (234 to 2700 R) and over the pressure range 0.01 to 100 atmospheres (0.15 to 1470 psia) by the Callery Chemical Company. These properties have been calculated from an equation of state derived from experimental P-V-T data on liquid and gaseous B_2H_6 (reported in Ref. 2.14 and 2.14a, respectively) which were weighted to minimize the standard deviation of the PV product. Using the weighted P-V-T data, the Callery Chemical Company derived coefficients for the Benedict-Webb-Rubin and Martin-Hou equations of state. It was found that the Benedict-Webb-Rubin equation can be fitted quite accurately to the superheated vapor points of the P-V-T data for B_2H_6, but cannot be fitted accurately to the data for both vapor and liquid. Because of this restriction to the superheated vapor alone, the simpler Martin-Hou equation was selected by Callery (Ref. 2.16) as the equation of state most representative of the available data.

Using the coefficients derived by Callery for the Benedict-Webb-Rubin equation of state, Rocketdyne (Ref. 2.17) calculated P-V-T properties for the superheated vapor. The resulting values deviated from those calculated by Callery (using the Martin-Hou equation) at the higher pressures (above 300 psia) and around the "dome" area.

There is some question as to which equation of state best represents the available B_2H_6 P-V-T data; however, this discrepancy can only be resolved with the generation of additional experimental P-V-T data, particularly for the liquid phase. Neither equation of state represents the saturated liquid density data for B_2H_6 as presented in Section 2.2.2.1. The more extensive calculations of Callery (Ref. 2.16) for the compressibility (Z = PV/RT) and density ratio (ρ/ρ_0) of the superheated vapor of diborane are presented in Tables 2.4 and 2.5, respectively.

2.2.2.6 Surface Tension. The surface tension of saturated liquid B_2H_6 has been determined by the methods of capillary rise (Ref. 2.11 and 2.13) and maximum bubble pressure (Ref. 2.12), and all three sets of experimental data are in reasonable agreement (the greatest difference at any temperature is less than 4 percent). Because there was no apparent reason for disregarding any of the work, all of the data were curve-fitted over the temperature range -129.5 to -69.7 C (-201.1 to -93.5 F, 143.7 to 203.5 K, or 258.6 to 366.2 R) to give the following equations:

$$\gamma_{(\mathrm{dynes/cm})} = 72.07 - 0.5152\, T_{(K)} + 1.055 \times 10^{-3}\, T_{(K)}^{2}$$

and

$$\gamma_{(\mathrm{lbf/ft})} = 4.939 \times 10^{-3} - 1.961 \times 10^{-5} T_{(R)} + 2.232 \times 10^{-8} T_{(R)}^{2}$$

These equations, graphically illustrated in Fig. 2.3 and 2.3a, have standard errors of estimate of 0.30 dynes/cm and 2.0×10^{-5} lbf/ft, respectively.

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2.2.2.7 Inert Gas Solubility. The solubilities of helium and nitrogen in B_2H_6 were measured (Ref. 2.18 and 2.19) at total pressures of 300 and 700 psia (20.4 and 47.6 atm) over the temperature range of -200 to -50 F (-129 to -46 C, 260 to 410 R, or 144 to 228 K). These solubility data for helium and nitrogen in B_2H_6 are plotted in Fig. 2.4 and 2.4a, respectively. The solubility of hydrogen in B_2H_6 was measured (Ref. 2.20) over a pressure range of about 4 to 42 atmospheres (60 to 600 psia) and temperatures ranging from 113.12 to 181.58 K (203.62 to 326.84 R, -160.03 to -91.57 C, or -256.05 to -132.83 F); the data from this study, evaluated and summarized in Ref. 2.19, are presented in Fig. 2.4b.

2.2.3 Thermodynamic Properties

The properties of B_2H_6 which define energy changes in the transitions through the various solid, liquid, and gas states, as well as in chemical changes, are classified under thermodynamic properties.

2.2.3.1 Heat of Formation. The heat of formation of B_2H_6 (ideal gas), as recommended by JANNAF (Ref. 2.21), is 9.8 ± 4.0 kcal/mole (638 ± 260 Btu/lb) at 298.15 K (536.67 R, 25.0 C, or 77.0 F). This value was derived from a weighted average of data reported in Ref. 2.22 through 2.29 and is based on the standard states of the elements (i.e., $B_{(c)}$ and $H_{2(g)}$ at 298.15 K).

The heat of formation of liquid B_2H_6 at its normal boiling point (180.6 K, 325.1 R, -92.6 C, or 134.7 F) was calculated, using the recommended JANNAF value of 9.8 kcal/mole for the heat of formation of the ideal gas at 298.15 K. The JANNAF Thermochemical Tables (Ref. 2.21) were used to compute the enthalpy change from the ideal gas at 298.15 K to the ideal gas at the normal boiling point, and the

Berthelot equation of state was used to compute the enthalpy change from the ideal to the real gas. Using these values and the heat of vaporization, the heat of formation of liquid B_2H_6 at its normal boiling point was then calculated to be 5.0 ±4 kcal/mole (325 ± 260 Btu/lb).

2.2.3.2 Heat of Fusion. The heat of fusion of B_2H_6 was measured calorimetrically (Ref. 2.3), with a resulting value of 1069 cal/mole (69.55 Btu/lb) at the melting point.

2.2.3.3 Heat of Vaporization. The heat of vaporization of B_2H_6 has been determined calorimetrically (Ref. 2.3 and 2.30) and from vapor pressure measurements (Ref. 2.3 and 2.4). All of the values are in excellent agreement, so an average value of 3413 cal/mole (222.0 Btu/lb) at the normal boiling point is recommended. In Ref. 2.30, additional values were determined calorimetrically from the normal boiling point to near the critical temperature. These data, shown in Fig. 2.5, can be represented by the expression:

$$\Delta H_v = 546.2 \left[T_c - T_{(K)}\right]^{0.39}$$

where ΔH_v = heat of vaporization, cal/mole

T_c = critical temperature, K

2.2.3.4 Heat Capacity. The heat capacity of solid B_2H_6 was determined experimentally (Ref. 2.3) from 13.83 to 104.558 K (24.89 to 188.204 R, -259.32 to -168.59 C, or -434.78 to -271.46 F). These data were curve-fitted with the following equations, represented graphically in Fig. 2.6 and 2.6a.

$$C_{p(cal/g\text{-}K)} = -0.155 + 1.123 \times 10^{-2} T_{(K)} - 8.150 \times 10^{-5} T_{(K)}^{2} + 3.137 \times 10^{-7} T_{(K)}^{3}$$

and

$$C_p(\mathrm{Btu/lb\text{-}R}) = -0.155 + 6.237 \times 10^{-3}T_{(R)} - 2.515 \times 10^{-5}T_{(R)}^{\;2} + 5.378 \times 10^{-8}T_{(R)}^{\;3}$$

The standard error of estimate for these equations is 0.002 cal/g-K (Btu/lb-R). However, it should be noted that all data points below 20 K (36 R) were excluded from the statistical evaluation because of difficulties in obtaining a good curve-fit over the entire range with a simple polynomial function.

The heat capacity of saturated liquid B_2H_6 was measured from 112.86 to 282.31 K (203.15 to 508.16 R, -160.29 to 916 C, or -256.52 to 48.49 F) in two sets of overlapping measurements (Ref. 2.3 and 2.6) which were in good agreement in the region of overlap. However, attempts to include all of the data points in the least-squares analysis produced poor curve-fits, even with higher order polynomials. This difficulty was caused by the abrupt change in curvature and increased scatter at the higher temperatures. After deleting the four highest temperature points, a good correlation was obtained from 113 to 263 K (203 to 473 R, -160 to -10 C, or -257 to 14 F). These correlations can be represented by the following equations:

$$C_{p(\mathrm{cal/g\text{-}K})} = 0.4266 + 4.358 \times 10^{-3}T_{(K)} - 2.353 \times 10^{-5}T_{(K)}^{\;2} + 2.05 \times 10^{-10}T_{(K)}^{\;4}$$

and

$$C_{p(\mathrm{Btu/lb\text{-}R})} = 0.4266 + 2.421 \times 10^{-3}T_{(R)} - 7.261 \times 10^{-6}T_{(R)}^{\;2} + 1.95 \times 10^{-11}T_{(R)}^{\;4}$$

The standard error of estimate for these equations, which are presented graphically in Fig. 2.7 and 2.7a, is 0.0062 cal/g-K (Btu/lb-R).

The heat capacity of the real gas B_2H_6 is discussed in Section 2.2.3.5 along with the other thermodynamic properties of B_2H_6 gas. Calculations of the ideal gas heat capacity (Ref. 2.31) are presented in Table 2.13 with the transport properties of the ideal gas.

2.2.3.5 Entropy and Enthalpy. Tables of the thermal functions for real gas B_2H_6 have been calculated by Callery Chemical Company (Ref. 2.16) and Rocketdyne (Ref. 2.17) using the equations of state discussed in Section 2.2.2.5. The same experimental P-V-T data (Ref. 2.14 and 2.14a), used to formulate these equations of state, were also used by other investigators (Ref. 2.32) to calculate entropy and enthalpy data for the superheated vapor from 0.5 to 30 atmospheres (7.35 to 441 psia) and 180.63 to 300 K (325.13 to 540 R), and for the compressed liquid from 10 to 60 atmospheres (147 to 882 psia) and 190 to 280 K (342 to 504 R). Because all of these data vary slightly due to differences in correlative techniques and weighting of the data, and additional experimental data would be required to establish a more accurate correlation, the more extensive data of Ref. 2.16 from 130 to 1500 K (234 to 2700 R) and 0.01 to 100 atmospheres (0.15 to 1470 psia) were arbitrarily selected for presentation. These calculated values for enthalpy, free energy, entropy, specific heat, specific heat ratio, and the Joule-Thompson coefficient of real gas B_2H_6 are presented in Tables 2.6 through 2.11, respectively.

The calculated data of Ref. 2.16 were also used as the basis for the thermal functions of the saturated liquid and vapor B_2H_6 presented in Table 2.12.

Using all of these data and other phase property and thermodynamic data presented in Sections 2.2.2 and 2.2.3, respectively, a "rough" temperature-entropy diagram (Fig. 2.8) has been drawn. A more detailed diagram is dependent on the establishment of additional experimental data.

2.2.4 Transport Properties

All properties of B_2H_6 that involve the transfer of mass or energy at the molecular level are presented in the following paragraphs.

2.2.4.1 Viscosity. The viscosity of saturated liquid B_2H_6 was measured with an Ostwald viscometer (Ref. 2.11) over the temperature range 145.6 to 203.9 K (262.1 to 367.0 R, -127.6 to -69.3 C, or -197.7 to -92.7 F). These data, plotted in Fig. 2.9 and 2.9a, were curve-fitted with the following equations:

$$\log \eta_{(cp)} = -2.027 + \frac{206.7}{T_{(K)}}$$

and

$$\log \eta_{(lbm/ft\text{-}sec)} = -5.199 + \frac{372.1}{T_{(R)}}$$

The standard error of estimate for these equations is 1.5 percent in η.

Calculations of viscosity of the ideal gas, reported in Ref. 2.31, are presented in Table 2.13.

2.2.4.2 Thermal Conductivity. There are no experimental thermal conductivity data for liquid B_2H_6. Calculated data, based on the method of Weber (Ref. 2.33), are reported in Ref. 2.34 and graphically illustrated in Fig. 2.10.

The translational, internal, and total thermal conductivities of the B_2H_6 ideal gas (as calculated in Ref. 2.31) are presented in Table 2.13.

2.2.4.3 Velocity of Sound. No data are available for the velocity of sound in either liquid or gaseous B_2H_6.

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2.2.4.4 Diffusivity. The diffusion coefficients for B_2H_6 vapors in nitrogen and helium gas have been determined as a function of temperature (Ref. 2.35). The diffusion coefficients obtained from this study are as follows:

Temperature				Diffusion Coefficient (D), cm^2/sec	
C	F	K	R	B_2H_6-He	B_2H_6-N_2
-77	-107	196	353	0.349	0.146
0	32	273	492	0.423	0.235
27	81	300	540	0.451	0.270
27	81	300	540	0.430 (calc.)	0.160 (calc.)

Although only a limited number of temperatures were used because of the difficulty in handling the material, the exponent m in the temperature dependence (T^m) of the diffusion coefficient (D), i.e., $D \propto T^m$, was calculated as 2.09 for B_2H_6 - He and 1.33 for B_2H_6 - N_2. It was felt that m varied somewhat from the expected value (i.e., 1.70 for most gases and vapors) due to decomposition of the B_2H_6, although steps were taken to minimize the impurities present.

2.2.5 Electromagnetic Properties

The electrical, magnetic, and electromagnetic (optical) properties of B_2H_6 have been grouped as "Electromagnetic Properties." These properties generally are related to the electronic structure of the atoms in contrast to the transport properties which involve only molecular movement.

2.2.5.1 Refractive Index. The refractive index of gaseous B_2H_6 was measured (Ref. 2.36) at 25 C (77 F, 298.15 K, or 536.67 R) and at wavelengths varying from 4359.56 A to 6440.24 A. A typical observed value of 1.00081832, measured at the mercury green line, has been reported in Table 2.1.

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No data or refractive index are reported for solid or liquid B_2H_6.

2.2.5.2 Dipole Moment. The dipole moment of B_2H_6 vapor was determined to be zero (Ref. 2.37). The absence of an electric moment indicates a symmetrical structure (see Section 2.4).

2.2.5.3 Dielectric Constant. The dielectric constant of saturated liquid B_2H_6 was measured (Ref. 2.4) over the temperature range 108.26 to 180.66 K (194.87 to 325.19 R, -164.89 to -92.49 C, or -264.80 to -134.48 F). These data, shown graphically in Fig. 2.11, can be represented by the equation:

$$\varepsilon = 2.3721 - 0.002765_3 T_{(K)}$$

The dielectric coefficient of B_2H_6 in the vapor state was measured (Ref. 2.37) at several temperatures. An average value is approximately 1.0018 at standard conditions. A more complete discussion of the results can be found in Ref. 2.38.

2.2.5.4 Electrical Conductivity. No electrical conductivity data have been reported for B_2H_6.

2.2.5.5 Magnetic Susceptibility. The magnetic suceptibility of gaseous B_2H_6 was measured (Ref. 2.39) with a High-Sensitivity (Pauling) Oxygen Meter, an instrument suitable for the quantitative comparison of the diamagnetic susceptibility of gases even at subatmospheric pressures. A molar value of $-21.0 \pm 0.8 \times 10^{-6}$, c.g.s., was obtained on a sample of questionable purity.

2.3 CHEMICAL PROPERTIES

2.3.1 General Characteristics

Diborane (B_2H_6) is a highly reactive chemical agent. It burns in air, and is completely hydrolyzed by water. It reacts readily with halogens, reactive metals, and various inorganic agents, and it enters into specific reactions with many organic compounds. Moreover, it undergoes facile thermal decomposition. This reactivity, coupled with toxicity, dictates special care in handling. On the other hand, it is this chemical reactivity that makes B_2H_6 a useful and important agent. Controlled oxidation of B_2H_6 is utilized in rocket propulsion; pyrolysis provides a means of obtaining pentaborane (B_5H_9) and decaborane ($B_{10}H_{14}$); and the reducing capacity, selectivity, and stereospecificity in organic systems mark B_2H_6 as a useful, specific synthetic reagent.

Reactions of B_2H_6 correlate with its bonding structure, electron deficiency, and polar character of the B-H linkage. The chemistry of B_2H_6 can be systematized on these structural grounds, as was done for boron hydrides in general by Parry and Edwards (Ref. 2.40). They divide reactions into four types: (1) symmetrical cleavage of the double bridge bonds, (2) nonsymmetrical cleavage, (3) loss of a proton from the bridge, and (4) loss of hydrogen gas from the molecule. A related basis for classification is provided by the chemical role of B_2H_6 in specific interactions: B_2H_6 can be considered as a Lewis acid, a reducing agent, and a precursor of higher boron compounds. The classification used here is based on the types of agents reacting with B_2H_6, and is more in keeping with practical objectives of this handbook. Although phenomenological aspects are stressed, some more interesting mechanistic features are pointed out; further details will be found in appropriate references.

The chemistry of B_2H_6 is dominated by bridge opening processes, and the reactions have generally been interpreted as those of borane(3), BH_3. Borane(3), or "borine," does not exist independently; it could not be isolated even in specially designed experiments at cryogenic temperatures (Ref. 2.41). But many stable adducts of borane with Lewis bases are well known, along with such derivatives as BF_3 and

$B(OR)_3$. Studies of the pyrolysis, isotopic exchange, and other reactions involving B_2H_6 have clearly established the equilibrium $B_2H_6 \rightleftharpoons 2\ BH_3$ as the initial step in many reactions (Ref. 2.42). Further justification for the frequent use of BH_3 or 1/2 B_2H_6 in chemical equations representing organic reactions of B_2H_6 is provided by the fact that these reactions are usually carried out in an ether as a solvent, with which B_2H_6 forms an adduct. In tetrahydrofuran (THF), for instance, B_2H_6 is known to exist as an adduct $THF:BH_3$ (Ref. 2.43).

The literature refers occasionally to diborane(4), B_2H_4, in addition to diborane(6), B_2H_6. Derivatives of diborane(4), such as B_2Cl_4 and $B_2(OR)_4$, are known and the existence of its complexes has been reported, but diborane(4) itself has never been isolated. We shall not discuss this rather hypothetical species, and in this handbook the unqualified term diborane means only diborane(6).

There have been a number of reviews of the chemistry of boron hydrides including B_2H_6 (Ref. 2.42 through 2.53). Stock's book (Ref. 2.44) describes his early pioneering work in Germany. A review book of Schechter et al. (Ref. 2.45) covers the chemistry of boron compounds up to 1954. Two more recent books are authoritative but rather confined: Lipscomb's book (Ref. 2.42) emphasizes topological aspects, while Brown's book (Ref. 2.43) is mainly concerned with organic reactions of boranes, or "hydroboration". A Russian review by Mikhailov (Ref. 2.49) deals specifically with B_2H_6. Much of the practical chemical information on B_2H_6 is contained in a book by Adams, published in 1964 (Ref. 2.50). The most recent reviews of the chemistry of boron hydrides are in books published in 1967 by Muetterties (Ref. 2.51), Mikhailov (Ref. 2.52), and Holzmann (Ref. 2.53).

The sections that follow describe typical reactions of B_2H_6. Usually, the products are highly dependent on the proportion of reactants, temperature, and other experimental conditions. For example, B_2H_6 and ammonia can yield either an adduct, or borazine, or borimide, depending on conditions. The necessity of consulting the original literature for details is, therefore, emphasized.

2.3.2 Pyrolysis

Diborane, like all the boron hydrides, is thermodynamically unstable at room temperature. Thermal decomposition becomes pronounced at fairly mild temperatures, around 100 C. Hydrogen is evolved, and condensed higher boron hydrides are formed; they decompose at progressively higher temperatures to give elemental boron at about 600 to 700 C.

Because most of the higher hydrides of boron are at present made from B_2H_6, its pyrolysis has been extensively studied. This work has been well summarized by both Adams (Ref. 2.50) and Holzmann et al. (Ref. 2.53). The earliest reported study was that in 1931 by Schlesinger and Burg (Ref. 2.54). Since then, many investigations have been carried out, using a shock tube (Ref. 2.55), a "hot-cold" reactor (Ref. 2.56), and a number of more conventional methods. The pyrolysis studies of Clark (Ref. 2.57), Clark and Pease (Ref. 2.58), Bragg (Ref. 2.59), Keilin (Ref. 2.60), Morrey and Hill (Ref. 2.61), Klein, et al. (Ref. 2.56), Eads and Murchinson (Ref. 2.62), Owen (Ref. 2.63), Norman (Ref. 2.64), Schaeffer (Ref. 2.65), Borer, et al. (Ref. 2.66), Enrione and Schaeffer (Ref. 2.67), Steward and Adler (Ref. 2.68), Clapper (Ref. 2.69), Hillman, et al. (Ref. 2.70), Fehlner and Koski (Ref. 2.55), and Baylis, et al. (Ref. 2.71) illustrate, chronologically, the approaches taken and the many problems encountered.

From these studies, most of which were directed at homogeneous decomposition in the gas phase, many contrasting mechanisms have been postulated indicating the complexity of the pyrolysis. The pyrolysis mechanism proposed by Clark (Ref. 2.57) was:

$$B_2H_6 \rightleftharpoons 2\ BH_3 \qquad (1)$$

$$BH_3 + B_2H_6 \rightleftharpoons B_3H_7 + H_2 \tag{2}$$

$$B_3H_7 + B_2H_6 \rightleftharpoons B_5H_{11} + H_2 \tag{3}$$

$$B_5H_{11} + H_2 \rightleftharpoons B_4H_{10} + BH_3 \tag{4}$$

$$B_4H_{10} + H_2 \rightleftharpoons 2\ B_2H_6 \tag{5}$$

$$B_4H_{10} \longrightarrow \text{polymer} + x\ H_2 \tag{6}$$

$$B_5H_{11} \longrightarrow \text{polymer} + y\ H_2 \tag{7}$$

$$B_5H_{11} \longrightarrow B_5H_9 + H_2 \tag{8}$$

$$B_5H_9 \longrightarrow \text{polymer} + z\ H_2 \tag{9}$$

Clark and Pease observed (Ref. 2.58) that the addition of hydrogen reduced the rate of disappearance of B_2H_6. Their postulated mechanism for the disappearance of B_2H_6 was:

$$B_2H_6 \rightleftharpoons 2\ BH_3 \tag{10}$$

$$BH_3 + B_2H_6 \xrightarrow{k_2} B_3H_7 + H_2 \tag{11}$$

$$B_3H_7 + H_2 \xrightarrow{k_3} B_2H_6 + BH_3 \tag{12}$$

$$B_3H_7 + B_2H_6 \xrightarrow{k_4} B_4H_{10} + BH_3 \tag{13}$$

with the following rate expression derived using the steady-state approximation:

$$\frac{d(B_2H_6)}{dt} = \frac{2k_2 \sqrt{K(k_4/k_3)}\ [B_2H_6]^{5/2}}{(k_4/k_3)\ [B_2H_6] + [H_2]} \tag{14}$$

This steady-state equation could be simplified to the form:

$$-\frac{dx}{dt} = k'\ P_o^{\ 1/2}\ x^{\ 5/2} \tag{15}$$

Eads and Murchison (Ref. 2.62) developed a mechanism explaining the many products formed in the pyrolysis of B_2H_6 and determined the rate constants and equilibrium constants involved in this mechanism. They represented the steps in the pyrolysis of B_2H_6 as:

$$B_2H_6 \rightleftharpoons 2\ BH_3 \tag{16}$$
$$B_2H_6 + BH_3 \rightleftharpoons (B_3H_9)^* \rightleftharpoons B_3H_7 + H_2 \tag{17}$$
$$B_3H_7 + BH_3 \rightleftharpoons (B_4H_{10})^* \rightleftharpoons B_4H_{10} \tag{18}$$
$$B_4H_{10} + BH_3 \rightleftharpoons (B_5H_{13})^* \rightleftharpoons B_5H_{11} + H_2 \tag{19}$$
$$B_3H_7 + B_2H_6 \rightleftharpoons (B_5H_{13})^* \rightleftharpoons B_5H_9 + 2\ H_2 \tag{20}$$
$$B_5H_{11} + BH_3 \rightleftharpoons (B_6H_{14})^* \rightleftharpoons B_6H_{10} + 2\ H_2 \tag{21}$$
$$B_6H_{10} + B_4H_{10} \rightleftharpoons (B_{10}H_{20})^* \rightleftharpoons B_{10}H_{14} + 3\ H_2 \tag{22}$$
$$B_{10}H_{14} + B_4H_{10} \rightleftharpoons B_9H_{11} + B_5H_{11} + H_2 \tag{23}$$
$$B_9H_{11} + B_4H_{10} \longrightarrow B_8H_8 + B_5H_{11} + H_2 \tag{24}$$
$$n\ B_8H_8 \longrightarrow (BH)_{8n} \tag{25}$$

where $(X)^*$ is an activated complex.

Schaeffer (Ref. 2.65) preferred the following mechanism for the pyrolysis of B_2H_6:

$$B_2H_6 \rightleftharpoons 2\ BH_3 \tag{26}$$
$$B_2H_6 + BH_3 \rightleftharpoons B_3H_9 \tag{27}$$
$$B_3H_9 \rightleftharpoons B_3H_7 + H_2 \tag{28}$$
$$B_3H_7 + B_2H_6 \rightleftharpoons B_4H_{10} + BH_3 \tag{29}$$
$$B_4H_{10} \rightleftharpoons B_4H_8 + H_2 \tag{30}$$
$$B_4H_8 + B_2H_6 \rightleftharpoons B_5H_{11} + BH_3 \tag{31}$$
$$B_5H_{11} \rightleftharpoons B_5H_9^* \tag{32}$$
$$B_5H_9^* + B_2H_6 \rightleftharpoons B_6H_{12} + BH_3 \tag{33}$$

Fehlner and Koski (Ref. 2.55), in their studies of the pyrolysis of B_2H_6 using a shock tube as a reactor, detected evidence for the existence of B_6H_{12}, B_7H_{11}, and B_7H_{13}. As a result, they proposed the following mechanisms:

$$B_2H_6 \rightleftharpoons 2\ BH_3 \tag{34}$$
$$BH_3 + B_2H_6 \rightleftharpoons B_3H_9 \tag{35}$$

$$B_3H_9 \rightleftharpoons B_3H_7 + H_2 \tag{36}$$

$$B_3H_7 + B_2H_6 \longrightarrow B_4H_{10} + BH_3 \tag{37}$$

$$B_3H_9 + B_2H_6 \longrightarrow B_5H_9 + 3\ H_2 \tag{38}$$

$$B_4H_{10} \rightleftharpoons B_3H_7 + BH_3 \tag{39}$$

$$B_4H_{10} \rightleftharpoons B_4H_8 + H_2 \tag{40}$$

$$B_4H_8 + B_2H_6 \longrightarrow B_5H_{11} + BH_3 \tag{41}$$

$$B_4H_8 + B_2H_6 \longrightarrow B_6H_{12} + H_2 \tag{42}$$

$$B_6H_{12} \rightleftharpoons B_6H_{10} + H_2 \tag{43}$$

$$B_5H_{11} \rightleftharpoons B_4H_8 + BH_3 \tag{44}$$

$$B_3H_7 + B_4H_{10} \longrightarrow B_7H_{13} + 2\ H_2 \tag{45}$$

$$B_7H_{13} \longrightarrow B_7H_{11} + H_2 \tag{46}$$

$$n\ B_4H_8 \longrightarrow m\ \text{(solid)} + p\ H_2 \tag{47}$$

Proposed mechanisms by Stewart and Adler (Ref. 2.68), used in deriving rate expressions, were as follows:

$$B_2H_6 \rightleftharpoons 2\ BH_3 \tag{48}$$

$$BH_3 + B_2H_6 \rightleftharpoons B_3H_9 \tag{49}$$

$$B_3H_9 \rightleftharpoons B_3H_7 + H_2 \tag{50}$$

$$B_3H_7 + B_2H_6 \longrightarrow B_5H_{11} + H_2 \tag{51}$$

$$B_3H_7 + B_2H_6 \longrightarrow B_4H_{10} + BH_3 \tag{52}$$

$$B_5H_{11} \longrightarrow B_4H_8 + BH_3 \tag{53}$$

$$B_4H_8 + H_2 \rightleftharpoons B_4H_{10} \tag{54}$$

$$B_4H_8 + B_2H_6 \longrightarrow B_5H_{11} + BH_3 \tag{55}$$

$$B_4H_{10} \longrightarrow B_3H_7 + BH_3 \tag{56}$$

$$B_5H_{11} \longrightarrow B_5H_9 + H_2 \tag{57}$$

$$B_5H_9 + B_3H_7 \longrightarrow B_8H_{14} + H_2 \tag{58}$$

$$B_8H_{14} \longrightarrow B_8H_{12} + H_2 \tag{59}$$

$$B_8H_{12} + B_2H_6 \longrightarrow B_{10}H_{16} + H_2 \tag{60}$$

$$B_{10}H_{16} \longrightarrow B_{10}H_{14} + H_2 \tag{61}$$

$$B_{10}H_{14} + BH_3 \longrightarrow B_{11}H_{15} + H_2 \tag{62}$$

$$B_{11}H_{15} + B_2H_6 \longrightarrow B_{12}H_{12} + BH_3 + 3\ H_2 \tag{63}$$

$$B_{12}H_{12} \longrightarrow \text{polymer} \tag{64}$$

These studies strongly indicated to Stewart and Adler "that the initial pyrolysis of B_2H_6 occurs by a 3/2-order reaction. The generally accepted interpretation is that B_2H_6 is in equilibrium with borane groups and that the rate-controlling step involves a species containing three boron atoms" (Ref. 2.53).

In his book, Lipscomb (Ref. 2.42) summarizes B_2H_6 pyrolysis studies around 100 C with the following sequence of reactions:

$$B_2H_6 \rightleftharpoons 2\ BH_3 \tag{65}$$

$$BH_3 + B_2H_6 \rightleftharpoons B_3H_9 \tag{66}$$

$$B_3H_9 \rightleftharpoons B_3H_7 + H_2 \tag{67}$$

$$B_3H_7 + B_2H_6 \rightleftharpoons B_4H_{10} + BH_3 \tag{68}$$

$$B_4H_{10} + BH_3 \rightleftharpoons B_5H_{11} + H_2 \tag{69}$$

$$B_4H_{10} + B_5H_{11} \rightleftharpoons B_5H_9 + 2\ B_2H_6 \tag{70}$$

He indicated reaction (67) is presumably rate-controlling, and may comprise more than one step. Since the process generates higher hydrides, Lipscomb (Ref. 2.42) deals with pyrolysis under the heating "Polymerization".

Holzmann et al. (Ref. 2.53) summarizes the technology of B_2H_6 pyrolysis as follows:

> "It is apparent that more work is needed to define the mechanism of pyrolysis of diborane to the higher boranes. However, a series of conclusions based on experimental studies can be stated. (1) Monoborane is an important species in the initial pyrolysis of diborane and in the formation of the higher boranes. (2) Other important pyrolysis intermediates include B_3H_7 and B_4H_8, although they have never been isolated or detected. (3) Various competing reactions lead to the formation of higher boranes making it difficult to interpret the kinetic data. (4) Both homogeneous and heterogeneous reactions occur in the pyrolysis process. (5) Catalytic activity of the pyrolysis products and reaction containers are [sic] not well defined."

In addition, Holzmann et al. (Ref. 2.53) summarizes the reaction orders and activation energies obtained in some of the B_2H_6 pyrolysis studies as follows:

Compound	Temperature, C	Initial Pressure, mm Hg	Reaction Order	Activation Energy (E_a), kcal/mole	Reference
B_2H_6	85-163	23-200	$\frac{3}{2}$	22.6	2.57
	85-163	23-200	$\frac{3}{2}$	26.0	2.58
	89-130	20-123	$\frac{3}{2}$	27.4 ±0.7	2.59
	80-110	20-123	$\frac{3}{2}$	25.5 ±0.5	2.59
	109-116.9	15-350	2	H_a = 36.7 ±4	2.61
	165-191	15-350	$\frac{3}{2}$	H_a = 32.4 ±2	2.61
	150	6	1	--	2.61
	101,131	100	1.35	22.5	2.64
	170-260	atmospheric	$\frac{3}{2}$	27.1	2.63
	90-126	--	$\frac{3}{2}$	22.1	2.68

In addition to production of pentaborane and decaborane, the thermal decomposition of B_2H_6 has been used to obtain boron-coated filaments (Ref. 2.72), and high-purity elemental boron (Ref. 2.73), at sufficiently high temperatures.

From the user's viewpoint, it is essential to remember that B_2H_6 undergoes a facile decomposition at relatively low temperatures, that products may accelerate further decomposition, and that some products, such as pentaborane, are more toxic and more hazardous than the original material.

2.3.3 Oxidation

Diborane burns in air, with a characteristic green flame, to give boric oxide and water (or boric acid):

$$B_2H_6 + 3\ O_2 \longrightarrow B_2O_3 + 3\ H_2O = 2\ B(OH)_3 \qquad (71)$$

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The high heat of combustion (514.4 kcal/mole), coupled with the wide flammability limits (0.9 to 98 m/o B_2H_6) and high flame speeds (20 to 100 times those of hydrocarbon flames) account for the use of B_2H_6 as a propellant.

Diborane-air mixtures containing 75- to 98-percent air detonate when sparked, the most violent explosion occurring in the mixture containing 90-percent air (Ref. 2.50).

Fehlner and Strong (Ref. 2.74) studied the gas-phase reaction between B_2H_6 and atomic oxygen. The products were hydrogen, tetraborane, pentaborane, and a white solid with the empirical formula BHO.

Studies on flammability, explosive oxidation, flame speeds, etc., are discussed by Adams (Ref. 2.50). More recent investigations of the oxidation of B_2H_6 include the work of Porter and Grimm on photochemical oxidation (Ref. 2.75), Breen and Zung on ignition (Ref. 2.76), and the oxidation studies by Carabine and Norrish using the flash photolysis technique (Ref. 2.77), all carried out in 1967 and 1968.

2.3.4 Hydrolysis and Alcoholysis

Diborane is rapidly and completely hydrolyzed by water, with copious generation of the hydrogen gas

$$B_2H_6 + 6\ H_2O \longrightarrow 2\ B(OH)_3 + 6\ H_2 \qquad (72)$$

A mechanism of the vapor-phase hydrolysis of B_2H_6 was proposed by Weiss and Shapiro (Ref. 2.78); also, a scheme for the hydrolysis of B_2H_6 outlined by Mochalov et al. (Ref. 2.79).

Diborane reacts with "bound water," e.g., hydroxyl groups on silica-gel surface, as follows (Ref. 2.80):

$$\text{-Si-OH} + B_2H_6 \longrightarrow \text{-Si-O-}B_2H_5 + H_2 \qquad (73)$$

The reaction has been utilized to measure the amount of hydroxyl groups attached to silicon and to aluminum in silica-alumina catalysts. Also, a treatment with B_2H_6 has been applied to modify properties of catalytic surfaces.

Diborane reacts with aqueous KOH as follows (Ref. 2.81):

$$2\ B_2H_6 + 4\ KOH \longrightarrow 3\ KBH_4 + KB(OH)_4 \qquad (74)$$

Jolly and Schmitt (Ref. 2.82) give evidence for the existence of BH_2^+ in acidic solutions, and of $BH(OH)_3^-$ in KOH solutions of B_2H_6.

Diborane reacts rapidly with methanol (Ref. 2.83). The overall reaction

$$B_2H_6 + 6\ CH_3OH \longrightarrow 2\ B(OCH_3)_3 + 6\ H_2 \qquad (75)$$

is analogous to that with water, but intermediate steps may be complex. A white by-product obtained by Burg and Schlesinger (Ref. 2.84) in the methanolysis of B_2H_6 may be polymeric methoxyborane, $(CH_3OBH_2)_n$.

From the user's viewpoint, it is essential to remember that in handling or storage of B_2H_6 moisture has to be rigorously excluded, and the contact of B_2H_6 with any materials having protons, -OH, or reducible organic functional groups has to be prevented.

2.3.5 Reactions With Nitrogen Compounds

Reactions of B_2H_6 with nitrogen compounds are dominated by adduct formation. As a Lewis acid, B_2H_6 complexes with bases. An analogy to coordinate compounds of the Werner type has been drawn (Ref. 2.40); the ligands NH_3, NH_2R, NHR_2 and NR_3 are common to the two cases. A certain paradox has been pointed out by Parry and Edwards: the Lewis acid BH_3 combines with another borane (Lewis acid) to give stable B_2H_6, hence borane groups may be considered as operational "electron deficient" bases as well as Lewis acids (Ref. 2.40).

Usually, with large bases, a symmetrical cleavage of the B_2H_6 bridge takes place

$$B_2H_6 + 2\ N(CH_3)_3 \longrightarrow 2\ BH_3{:}N(CH_3)_3 \qquad (76)$$

but with smaller bases, an asymmetric cleavage may occur

$$B_2H_6 + 2\ NH_3 \longrightarrow (NH_3)_2BH_2^{+}BH_4^{-} \qquad (77)$$

The above shown product of the reaction of B_2H_6 with ammonia (at low temperatures) is referred to in the earlier literature as the "diammoniate of diborane," $B_2H_6(NH_3)_2$. The ammonia-borane adduct (as if originating from the symmetrical cleavage) can be prepared but by a different route, namely the reaction of ammonium salts with borohydrides

$$NH_4^{+} + BH_4^{-} \longrightarrow BH_3{:}NH_3 + H_2$$

Reactions of B_2H_6 with specific nitrogen compounds are well covered in several reviews (Ref. 2.45 and 2.50), while properties of the adducts are treated extensively by Stone (Ref. 2.47). Examples of reactions follow.

$B_2H_6 + 2\ NH_3 \xrightarrow{-150\ C} B_2H_6(NH_3)_2 \left[= (NH_3)_2BH_2^{+}BH_4^{-}\right]$ (78) (Ref. 2.44)

$B_2H_6(NH_3)_2 \xrightarrow{200\ C} B_3N_3H_6 + H_2 + (BNH_2)_n$ (79) (Ref. 2.44)
borazine, "inorganic benzene"

$3\ B_2H_6 + 6\ NH_3 \xrightarrow{200\ C} 2\ B_3N_3H_6 + 12\ H_2$ (80) (Ref. 2.45)
$B_2H_6 + 3\ NH_3 \longrightarrow B_2(NH)_3 + 6\ H_2$, borimide (81) (Ref. 2.45)
$B_2H_6 + 2\ RNH_2 \longrightarrow 2\ BH_3\!: NH_2R$ (82) (Ref. 2.50)
$B_2H_6 + 2\ R_2NH \longrightarrow 2\ BH_3\!:NHR_2$ (83) (Ref. 2.50)
$B_2H_6 + 2\ R_3N \quad 2\ BH_3\!:NR_3$ (84) (Ref. 2.50)

$B_2H_6 + N_2H_4 \xrightarrow{-80\ C} BH_3\!:NH_2NH_2\!:BH_3$ (85) (Ref. 2.85)
$BH_3\!:N_2H_4$ has also been reported (86) (Ref. 2.51)
$BH_4^{-} + NH_4^{+} \longrightarrow BH_3\!:NH_3 + H_2$ (87) (Ref. 2.50)

$BH_4^{-} + N_2H_5^{+} \longrightarrow BH_3\!:N_2H_4 + H_2$ (88) (Ref. 2.86)

$B_2H_6 + 2\ C_6H_5N \xrightarrow{0\ C} 2\ C_6H_5N\!:BH_3$ (89) (Ref. 2.43)

$B_2H_6 + 2\ RCN \xrightarrow{-80\ C} 2\ BH_3\!:NCR \xrightarrow{25\ C}$ polymer (90) (Ref. 2.50)

$B_2H_6 + 2\ NH_2OH \xrightarrow{-112\ C} (BH_3\!:NH_2OH)_n \xrightarrow{25\ C}$ a white solid (91) (Ref. 2.50)

The reaction of B_2H_6 with pyridine, followed by displacement with BF_3, has been used as a means of purification of B_2H_6 Lauer. (Ref. 2.87) has patented the use of hydrazine-boron hydride mixtures for removing carbon deposits in internal combustion engines.

2.3.6 Reactions With Halogens and Halogen Compounds

Reactions of B_2H_6 with halogens and hydrogen halides were studied early by Stock (Ref. 2.44). Reactions lead to terminal substitution and the formation of boron trihalides. Free chlorine is the most reactive agent. Examples of reactions follow.

$B_2H_6 + Cl_2 \longrightarrow$ explosion, BCl_3 found (92) (Ref. 2.44)
$B_2H_6 + Br_2 \xrightarrow{100\ C} B_2H_5Br$, also BBr_3 (93) (Ref. 2.44)

$B_2H_6 + I_2 \longrightarrow BI_3$ + oily substances (94) (Ref. 2.44)

B_2H_6(pure) + HCl $\xrightarrow{25\ C}$ no reaction (95) (Ref. 2.50

$B_2H_6 + HBr \xrightarrow{90\ C} B_2H_5Br$, BBr_3 and H_2 (96) (Ref. 2.50)

$B_2H_6 + HI \longrightarrow B_2H_5I + H_2$ (97) (Ref. 2.50)

An azeotrope, formed from 70.1 percent B_2H_6 and 29.9 percent HCl, boils at -94 C; another azeotrope, containing 41.6 percent B_2H_6 and 58.4 percent BF_3, boils at -106 C (Ref. 2.88).

Recent (1967-1968) studies of the reactions of B_2H_6 with BCl_3 and BBr_3 were conducted by Bouis and Cueilleron in France (Ref. 2.89 and 2.89a). With BBr_3, the products were $BHBr_2$ and B_2H_5Br; analogous products were obtained with BCl_3.

2.3.7 Reactions With Metals, Metal Hydrides, and Metal Salts

Being electron-deficient, boranes will accept electrons from active metals under suitable reaction conditions; borohydrides are obtained. The reactivity of metal salts and metal hydrides varies considerably. Often, the course depends on "suitable reaction conditions". Thus, a 1954 review (Ref. 2.45) states that neither NaH nor KH have been made to react with B_2H_6, but the 1962 book by Brown (Ref. 2.43) refers to the NaH-B_2H_6 reaction as a facile one in an appropriate solvent (diglyme) at 25 C. Examples of reactions studied are given below:

$2\ B_2H_6 + 2\ Na \longrightarrow NaBH_4 + NaB_3H_8$ (98) (Ref. 2.90)

$B_2H_6 + 2\ LiH \longrightarrow 2\ LiBH_4$ (99) (Ref. 2.43)

$B_2H_6 + 2\ NaH \xrightarrow{25\ C} 2\ NaBH_4$ (100) (Ref. 2.43)

$B_2H_6 + NaH \longrightarrow NaB_2H_7$ (= $NaBH_4 \cdot BH_3$) (101) (Ref. 2.43)

$2\ B_2H_6 + LiAlH_4 \longrightarrow LiBH_4 + Al\ (BH_4)_3$ (102) (Ref. 2.50)

$2\ B_2H_6 + Al(CH_3)_3 \xrightarrow{80\ C} Al(BH_4)_3 + B(CH_3)_3$ (103) (Ref. 2.50)

$1/2\ B_2H_6 + KF \longrightarrow KBH_3F$ (104) (Ref. 2.91)

$B_2H_6 + NaCN \longrightarrow NaBH_3CNBH_3$ (105) (Ref. 2.50)

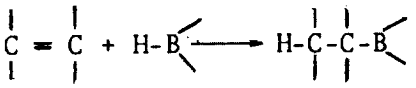
$2\ B_2H_6 + 3\ NaOCH_3 \longrightarrow 3\ NaBH_4 + B(OCH_3)_3$ (106) (Ref. 2.92)

$B_2H_6 + NaNO_2 \xrightarrow{200\ C}$ no reaction (107) (Ref. 2.43)

2.3.8 Reactions With Organic Compounds

With paraffins, B_2H_6 does not react (practically) below 180 C. However, B_2H_6 adds to the double bonds of olefins and acts as a selective reducing agent for several classes of organic compounds.

Addition of B_2H_6 to olefins was studied in 1948 by Hurd (Ref. 2.93); the reaction appeared slow and required elevated temperatures. Reexamination of the reaction by Brown and Subba Rao in 1956 (Ref. 2.94) revealed that the reaction is catalyzed remarkably by ethers. Ethers, such as diglyme (dimethyl ether of diethylene glycol) or tetrahydrofuran, THF, are used as solvents. The reaction has been termed "hydroboration".



(108)

Brown has written a book dealing extensively with this particular reaction (Ref. 2.43). Hydroboration, HB, is applicable to multiple bonds between carbon and carbon, nitrogen or oxygen. Olefins yield trialkylboranes

$$6\ RC = CH_2 + B_2H_6 \xrightarrow{THF} 2\ B(CH_2CH_2R)_3 \qquad (109)$$

The reaction shows stereospecificity, giving cis addition, and is anti-Markowinkoff. Hydroboration offers a convenient route for some syntheses.

Thus, hydroboration followed by protonolysis with a carboxylic acid gives a procedure for the hydrogenation of double bonds (Ref. 2.95). Hydroboration followed by oxidation provides a valuable means for the anti-Markownikoff hydration of olefins (i.e., obtaining a primary alcohol):

$$\mathrm{RCH{=}CH_2} \xrightarrow{\mathrm{HB}} \mathrm{RCH_2CH_2{-}B}\begin{smallmatrix}/\\ \backslash\end{smallmatrix} \xrightarrow{[\mathrm{O}]} \mathrm{RCH_2CH_2OH} \tag{110}$$

Diborane is a selective reducing agent. It reduces aldehydes, ketones, nitriles, esters, and other types of compounds. Especially remarkable is the rapid reduction of the normally stable carboxylic acids. Some standard organic substrates and their products from reaction with B_2H_6 are as follows (Ref. 2.43):

Aldehyde → Alcohol (111)
Ketone → Alcohol (112)
Acid Chloride → No reaction (113)
Lactone → Glycol (114)
Oxide → Alcohol (115)
Ester → Alcohol (slow) (116)
Carboxylic Acid → Alcohol (fast) (117)
Nitrile → Amine (118)
Nitro → No reaction (119)
Olefin → Organoborane (fast) (120)
Carboxylic salt → No reaction (addition only) (121)

Brown and Korytnyk (Ref. 2.96) found that the rates of reduction by B_2H_6 decrease in the order: carboxylic acids > olefins > ketones > nitriles > epoxides > esters > acid chlorides. This order is markedly different from that for alkali metal borohydride (for which acid chlorides are most reactive, and carboxylic acids are least reactive).

Diborane causes some polymerization of vinyl compounds, such as acrylonitrile, methylmethacrylate and styrene (Ref. 2.50).

Recent studies with B_2H_6 include reduction of Schiff bases, by Japanese workers (Ref. 2.97); reduction of oximes (Ref. 2.98); reduction of aromatic aldehydes and ketones, in England (Ref. 2.99); reduction of polyfluorinated olefins (Ref. 2.100); hydroxylation of diene polymers (Ref. 2.101); reaction of organic acid amides, studied in Russia (Ref. 2.102); and gas phase hydroboration (Ref. 2.103). The most recent (1969) study is an interesting work of Atassi and Rosenthal on the specific reduction of -COOH in peptides and proteins (Ref. 2.104).

2.3.9 Miscellaneous Reactions

Some reactions of B_2H_6 not included in previous sections are given below:

Adduct Formation with Oxygen-Containing Bases

$B_2H_6 + 2\,(CH_3)_2O \xrightarrow{-78\ C} 2\ BH_3{:}O(CH_3)_2$ (122) (Ref. 2.50)

$B_2H_6 + 2\,CO \longrightarrow 2\ BH_3{:}CO$ (123)

$B_2H_6 + 2\ C_4H_8O \longrightarrow 2\ BH_3{:}OC_4H_8$ (124) (Ref. 2.43)

Adduct Formation with Group V Bases

$B_2H_6 + LiNH_2 \longrightarrow LiBH_4 + \frac{1}{n}(BH_2NH_2)_n$ (125) (Ref. 2.50)

$B_2H_6 + 2\ PH_3 \longrightarrow 2\ BH_3{:}PH_3$, analogous to NH_3 (126) (Ref. 2.50)

$B_2H_6 + 2\ CH_3PH_2 \xrightarrow{-78\ C} 2\ BH_3{:}PH_2CH_3$ (127) (Ref. 2.50)

$B_2H_6 + 2\ PF_3 \longrightarrow 2\ BH_3{:}PF_3$ (128) (Ref. 2.50)

$B_2H_6 + 2\ AsH(CH_3)_2 \xrightarrow{-78\ C} 2\ BH_3{:}AsH(CH_3)_2$ (129) (Ref. 2.105)

$B_2H_6 + (CH_3)_4Sb_2 \longrightarrow 2\ (CH_3)_2SbBH_2 + H_2$ (130) (Ref. 2.106)

$B_2H_6 + 2\ (C_6H_5)_2C{=}NH$ (diphenyl Ketimine) $\longrightarrow 2BH_3{:}NH{=}C(C_6H_5)_2$

(131) (Ref. 2.107)

Reactions with Oxygen-Containing Compounds

$B_2H_6 + 4\ R_2CO \longrightarrow 2\ (R_2HCO)_2\ BH$ (132) (Ref. 2.50)

$B_2H_6 + CO \longrightarrow$ trimethylboroxine (133) (Ref. 2.108)

$B_2H_6 + C_4H_8O \xrightarrow{60\ C} (C_4H_9O)_3B$ (134) (Ref. 2.109)

$B_2H_6 + 2\ RCOO^-(\text{salt}) \longrightarrow 2\ RC(O)OBH_3^-$ (135) (Ref. 2.50)

Distribution Reactions

$B_2H_6 + B(CH_3)_3 \xrightarrow{80\ C} B_2H_5CH_3,\ B_2H_4(CH_3)_2,$ etc. (136)

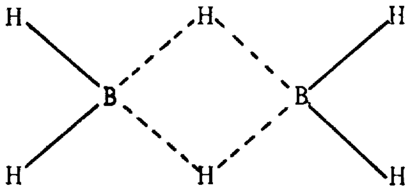
$B_2H_6 + B_2D_6 \longrightarrow B_2DH_5,\ B_2D_2H_4,$ etc. (137)

$2\ B_2H_6 + 3\,C_2H_5MgCl \xrightarrow{C_4H_8O} 3\,ClMgBH_4 \cdot 2\ C_4H_8O + B(C_2H_5)_3$

(138) (Ref. 2.110)

2.4 STRUCTURE AND SPECTRA

The molecular structure of B_2H_6 was a subject of controversy for many years. Early electron diffraction studies suggested an ethane-like structure, H_3B-BH_3, while later evidence and interpretation suggested a structure involving hydrogen bridges between the boron atoms:



The now-accepted hydrogen-bridge model was first proposed by Dilthey (Ref. 2.111) and firmly established by infrared measurements (Ref. 2.112 and 2.113) and electron diffraction studies (Ref. 2.114).

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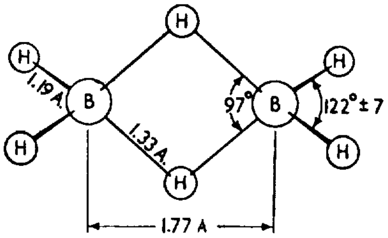
Much additional evidence has supported the bridge structure. A diagram and parameters for the bridge model are given below (Ref. 2.115):



The boron atoms and the four terminal hydrogen atoms lie in the same plane, while the two bridging hydrogen atoms lie symmetrically above and below this plane. Thus, each boron atom is surrounded by four hydrogen atoms in a tetrahedral arrangement.

2.5 MIXTURES AND GELS

3.5.1 Mixtures

No data have been reported for potential or practical propellant mixtures containing B_2H_6.

2.5.2 Gels

As a part of NASA's consideration of gelled propellants for deep space missions, studies are being conducted to gel and characterize (gelled) B_2H_6. This interest in gelled propellants is based on potential advantages of: (1) positional stability in a zero-g environment, and (2) reduced sloshing. Possible disadvantages are: (1) reduction in performance, and (2) an impairment in restart capability if an inert, high-melting particulate material is used as the gelling agent.

In initial studies (Ref. 2.116) to gel B_2H_6 with fine particles of a volatile fuel, the use of trimethylamino compounds was

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investigated. Trimethylaminoborane particles were prepared in liquid methane by the following reaction:

$$B_2H_6 + 2(CH_3)_3N \longrightarrow 2(CH_3)_3NBH_3$$

The liquid methane was sparged off and replaced with liquid B_2H_6; vigorous stirring resulted in an "excellent gel" of the B_2H_6.

More detailed characterization of the trimethylaminoborane-based gels of B_2H_6 in a continuation of the program (Ref. 2.117) indicated that these gels did not meet selected storage requirements. As a result, other candidate gellants were tested, and 3 to 4 weight percent trimethylaminoboron trifluoride was successfully used to gel B_2H_6. The trimethylaminoboron-trifluoride-based B_2H_6 gels have been stored at 250 R for 30 days and at 280 R for 2 days with no evidence of stability degradation. Additional physical and engineering characterization of these gels is in progress (Ref. 2.117).

The potential detrimental effects of gel-like formation in B_2H_6 flow systems have been considered as part of a study (Ref. 2.118) to investigate the formation and behavior of clogging materials in space-storable propellants. The investigators in this study reported that earlier investigators, in attempting to destroy aluminum chloride catalysts in Friedel-Crafts alkylation experiments with boron hydrides under the High Energy Liquid Boron Hydrides Program (ZIP), found that partially hydrolyzed aluminum chloride acted as a gelling agent for boron hydrides. They also reported (Ref. 2.118) that ferric chloride is a similar catalytic material which can react with water to form hydrated colloidal particles, and that the reaction of B_2H_6 with this class of materials would be a suspected source of gel-like structures that might result in possible flow decay or stoppage in convenient points (e.g., filters, orifices, etc.) in B_2H_6 systems.

2.6 HEAT TRANSFER PROPERTIES

2.6.1 Forced Convection

Very few data have been published on the heat transfer characteristics of B_2H_6 under conditions in which it could be used as a regenerative coolant. In an in-house experimental program at Rocketdyne (Ref. 2.119), heated-block heat transfer tests were conducted with both liquid and gaseous B_2H_6 under conditions similar to a pressure-fed regeneratively cooled engine. Mass velocities were run in the range of 0.5 to 3.0 $\mathrm{lb/in.^2}$-sec with coolant inlet pressures from 50 to 400 psia. A total test duration of 750 seconds was accumulated with wall temperatures from 70 to 600 F. The results of these tests, summarized in Fig. 2.12 and 2.13 as Stanton Number and Nusselt Number correlations, respectively, can be correlated by the following relation.

$$N_{Nu_B} = 0.023\, N_{Re_B}^{\ 0.8} N_{Pr_B}^{\ 0.4}$$

where the properties are evaluated under bulk (B) conditions and

N_{Nu_B} = Nusselt Number = $\frac{h\ D}{k}$

N_{Re_B} = Reynolds Number = $\frac{DV\rho}{\mu}$

N_{Pr_B} = Prandtl Number = $\frac{C_p\mu}{k}$

h = heat transfer coefficient

D = characteristic length

k = thermal conductivity

V = velocity

ρ = density

C_p = heat capacity at constant pressure.

μ = viscosity

A current program is being conducted by Rocketdyne under Contract NAS7-765 (Ref. 2.120) to study, design, fabricate, and demonstrate a regeneratively cooled rocket engine using OF_2/B_2H_6.

2.6.2 Film Cooling

Studies were performed at Aerojet-General Corporation (Ref. 2.121) to evaluate B_2H_6 as a liquid film coolant. In these studies, liquid B_2H_6 was injected onto a thin preheated stainless-steel strip. Gaseous nitrogen flowing at 60 ft/sec over the film was used to simulate the shear forces produced by the flow of combustion gases. The plate temperature was measured as a function of time, and visual observations were made using high-speed photography. Heat fluxes were obtained by performing an energy balance on the plate.

The normal heat transfer mechanisms are indicated at wall temperatures lower than 1000 F. Nucleate boiling and forced convection mechanisms predominate up to 150 F. A transition zone occurs from 150 to 300 F in which boiling-like behavior is evident. From 300 to 1000 F, film boiling takes place and the heat flux increases slowly with temperature. These three zones are clearly evident in Fig. 2.14 (taken from Ref. 2.121), when experimental values of heat flux are plotted as a function of wall temperature. From 1000 to 1300 F, the highest temperatures studied, decomposition of the B_2H_6 occurred as characterized by deposits of elemental boron on the plate following a run.

A current program in the area of film cooling using B_2H_6 is being conducted by Rocketdyne under Contract NAS7-767 (Ref. 2.122). The objective of this program is to advance and extend the technology of boundary/conduction-cooled rocket thrust chambers to the OF_2/B_2H_6 propellant system.

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2.7 IGNITION CHARACTERISTICS

Several ignition studies have been conducted for the propellant combination OF_2/B_2H_6 at both sea level and altitude conditions (Ref. 2.123 through 2.128). These propellants have been shown to be hypergolic in both the liquid and gas phases.

RMD studies (Ref. 2.123) showed that the OF_2/B_2H_6 combination is reliably hypergolic from sea level to a simulated altitude of 87,000 feet. Ignition occurred in the gas phase in the simulated altitude tests, and delay times were short and chamber pressure rise smooth. Ignition delay times of 9 to 15 milliseconds were observed for the gaseous propellants (independent of altitude), while ignition delays for the liquid propellants were somewhat higher under similar conditions. It was also found that chamber and injector configurations, temperature, propellant leads, mixture ratio, etc., had little effect on ignition characteristics at altitude, while injector design and liquid phase mixing had significant effects.

Tests conducted at Aerojet at about the same time (Ref. 2.124), for the liquid OF_2/B_2H_6 system with mixture ratios varying from 0.2 to 40, also showed rapid hypergolic ignition, accompanied by generally smooth initial and sustained chamber pressure.

Ignition studies conducted by the Air Force (Ref. 2.125) showed smooth and repeatable hypergolic ignition in larger engines for liquid phase OF_2/B_2H_6, but excessive ignition delays and generally hard starts were obtained for gaseous OF_2/B_2H_6.

More recent investigations at RMD (Ref. 2.126 and 2.127) have been conducted to determine the vacuum ignition characteristics of both OF_2/B_2H_6 and FLOX (70-30)/B_2H_6. The ignition delays of FLOX/B_2H_6 in 100-pound-thrust engines fired at simulated altitudes in excess of 250,000 feet were found to be slightly shorter than those for OF_2/B_2H_6 (22.5 ± 1.5 versus 26 ± 1 milliseconds) under comparable conditions (Ref. 2.126. and 2.127). The dominant ignition reactions appear to be gas-phase, so that the shorter delays for $FLOX/B_2H_6$ may be attributed to the higher vapor pressure of the FLOX and the fluorine-enriched vapor, which results from preferential vaporization of fluorine. It was also found that the shortest ignition delays for both propellant combinations occurred with a no-lead condition.

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TABLE 2.1

PHYSICAL PROPERTIES OF DIBORANE

Property	Value		Figure Number	Reference Number
	Metric	English		
<u>General Identification</u>				
Identification	Diborane			
Molecular Formula	B_2H_6			
Molecular Weight	27.668			2.2
Melting Point	108.30 K (-164.85 C)	194.94 R (-264.73 F)		2.3, 2.4
Triple Point	108.30 K (-164.85 C)	194.94 R (-264.73 F)		2.3, 2.4
Normal Boiling Point	180.5 K (-92.6 C)	325.0 R (-134.7 F)		-
Critical Properties				
Temperature	289.9 K (16.7 C)	521.8 R (62.1 F)		2.9
Pressure	39.5 atm	581 psia		2.9
Density	0.163 g/cc *	10.2 lb/cu ft *		-
Volume	6.144 cc/g *	0.0984 cu ft/lb *		2.6
<u>Phase Properties</u>				
Density				
Solid	0.577 g/cc at 90 K	36.02 lb/cu ft at 162 R		2.10
Liquid	0.436 g/cc at NBP	27.21 lb/cu ft at NBP	2.1,2.1a 2.1d	2.11,2.12,2.13
Gas	1.92 x 10^3 g/cc at NBP	0.120 lb/cu ft at NBP	2.1b,2.1c 2.1d	2.14a
Thermal Expansion(cubic)	2.44 x 10^{-3}/K at NBP, 10 atm	1.36 x 10^{-3}/R at NBP, 147 psia	Table 2.2	2.14

*Calculated data

TABLE 2.1 (Continued)

Property	Value		Figure Number	Reference Number
	Metric	English		
Compressibility				
Adiabatic	---	---		
Isothermal (liquid)	See Tables 2.3, 2.3a			2.11,2.14
Vapor Pressure	6.8 atm at 224.2 K	100 psia at 403.6 R	2.2,2.2a	2.3,2.4 2.6,2.7 2.8
PVT Properties (gas)	See Tables 2.4 and 2.5			2.16
Surface Tension	13.45 dynes/cm at NBP	9.22×10^{-4} lbf/ft at NBP	2.3,2.3a	2.11,2.12 2.13
Inert-Gas Solubility				
Helium	See Fig. 2.4		2.4	2.18,2.19
Nitrogen	See Fig. 2.4a		2.4a	2.18,2.19
Hydrogen	See Fig. 2.4b		2.4b	2.19,2.20
Thermodynamic Properties				
Heats of				
Formation				
Liquid	5.0 kcal/mole at NBP*	325 Btu/lb at NBP*		
Ideal Gas	9.8 kcal/mole at 298.15 K*	637.5 Btu/lb at 536.67 R*		2.21
Fusion	1069 cal/mole at MP	69.55 Btu/lb at MP		2.3
Vaporization	3413 cal/mole at NBP	222.0 Btu/lb at NBP	2.5	2.3,2.4, 2.30

*Calculated data

TABLE 2.1 (Continued)

Property	Value		Figure Number	Reference Number
	Metric	English		
Heat Capacity				
Solid	0.489 cal/g-K at 105 K	0.489 Btu/lb-R at 189 R	2.6,2.6a	2.3
Liquid	0.6642 cal/g-K at NBP	0.6642 Btu/lb-R at NBP	2.7,2.7a	2.3,2.6
Gas	See Section 2.2.3.5			2.16
Entropy	See Section 2.2.3.5		2.8	2.16
Enthalpy	See Section 2.2.3.5		2.8	2.16
<u>Transport Properties</u>				
Viscosity				
Liquid	0.131 centipoise at NBP	8.82 x 10^{-5} lbm/ft-sec at NBP	2.9,2.9a	2.11
Gas	See Table 2.13			2.31
Thermal Conductivity				
Liquid	2.62 x 10^{-3} g-cal/sec-cm-C at 178 K*	0.634 Btu/ft-hr-F at 320 R*	2.10	2.34
Gas	See Table 2.13			2.31
Sonic Velocity				
Liquid	---	---		
Gas	---	---		
Diffusion Coefficient	See Section 2.2.4.4			2.35
<u>Electromagnetic Properties</u>				
Index of Refraction				
Solid	---	---		
Liquid	---	---		
Gas	$\eta_{5462.25A}$ = 1.00081832 at 298.15 K (536.67 R)			2.36

*Calculated data

Table 2.1 (Concluded)

Property	Value		Figure Number	Reference Number
	Metric	English		
Electromagnetic Properties (Continued)				
Dipole Moment (vapor)	0 Debye units			2.37
Dielectric Constant				
Liquid	1.8728 at NBP		2.11	2.4
Gas	1.0018 at STP			2.37,2.38
Electrical Conductivity				
Magnetic Susceptibility	$\chi_M = -210 \pm 0.8 \times 10^{-6}$, c.g.s.			2.39

TABLE 2.2

COEFFICIENTS OF THERMAL EXPANSION (CUBIC) FOR DIBORANE (REF. 2.14)

Temperature		Pressure		$\alpha \times 10^3$	
K	R	atm	psia	K	R
180.63	325.13	10	147	2.44	1.36
		20	294	2.42	1.34
		30	441	2.40	1.33
		40	588	2.38	1.32
		50	735	2.36	1.31
		60	882	2.34	1.30
190	342	10	147	2.65	1.47
		20	294	2.62	1.46
		30	441	2.59	1.44
		40	588	2.56	1.42
		50	735	2.53	1.41
		60	882	2.50	1.39
200	360	10	147	2.93	1.63
		20	294	2.88	1.60
		30	441	2.83	1.57
		40	588	2.78	1.54
		50	735	2.73	1.52
		60	882	2.68	1.49
212.5	382.5	10	147	3.26	1.81
		20	294	3.19	1.77
		30	441	3.12	1.73
		40	588	3.05	1.69
		50	735	2.98	1.66
		60	882	2.91	1.62

TABLE 2.2 (Concluded)

Temperature		Pressure		$\alpha \times 10^3$	
K	R	atm	psia	K	R
225	405	10	147	3.88	2.16
		20	294	3.72	2.07
		30	441	3.61	2.01
		40	588	3.50	1.94
		50	735	3.39	1.88
		60	882	3.28	1.82
237.5	427.5	20	294	4.45	2.47
		30	441	4.20	2.33
		35	515	4.07	2.26
		40	588	3.98	2.21
		50	735	3.79	2.11
		60	882	3.63	2.02
250	450	20	294	5.74	3.19
		30	441	5.28	2.93
		35	515	5.08	2.82
		40	588	4.88	2.71
		50	735	4.50	2.50
		60	882	4.22	2.34
262.5	472.5	30	441	6.64	3.69
		35	515	6.38	3.54
		40	588	5.95	3.31
		50	735	5.39	2.99
		60	882	4.96	2.76
273.15	491.67	30	441	11.20	6.22
		35	515	8.94	4.97
		40	588	7.94	4.41
		50	735	6.71	3.73
		60	882	5.89	3.27

TABLE 2.3
LIQUID DIBORANE COMPRESSIBILITY (Ref. 2.11)

Temperature		Pressure		Density	
K	R	atm	psia	g/cc	lb/cu ft
243.6	438.5	18.2	268	0.337	21.04
		21.0	309	0.337	21.04
		27.9	410	0.338	21.10
		63.1	927	0.348	21.73
250.0	450.0	26.7	393	0.324	20.23
		61.2	900	0.332	20.73
256.1	461.0	31.9	469	0.314	19.60
		66.5	977	0.334	20.85
268.1	482.6	25.2	370	0.286	17.85
		32.9	484	0.299	18.67
		61.4	902	0.317	19.79
275.8	496.4	42.3	622	0.281	17.54
		68.7	1010	0.299	18.67
277.8	500.0	43.7	642	0.272	16.98
		69.5	1022	0.295	18.42
284.1	511.4	52.2	767	0.266	16.61
		68.2	1002	0.284	17.73
287.1	516.8	52.9	777	0.257	16.04
		72.5	1065	0.279	17.42

TABLE 2.3a
ISOTHERMAL COMPRESSIBILITY OF LIQUID DIBORANE (β) (Ref. 2.14)

Temperature		Pressure		$\beta \times 10^4$	
K	R	atm	psia	atm^{-1}	$psia^{-1}$
180.63	325.13	60	882	2.33	0.159
		50	735	2.33	0.159
		40	588	2.34	0.159
		30	441	2.34	0.159
		20	294	2.35	0.160
		10	147	2.35	0.160
		1.0000	14.7	2.36	0.161
190	342	60	882	2.95	0.201
		50	735	2.95	0.201
		40	588	2.96	0.201
		30	441	2.97	0.202
		20	294	2.97	0.202
		10	147	2.98	0.203
		1.6358	24.05	2.99	0.203
200	360	60	882	2.44	0.166
		50	735	2.55	0.174
		40	588	2.66	0.181
		30	441	2.80	0.191
		20	294	2.95	0.201
		10	147	3.13	0.213
		2.6084	38.34	3.29	0.224
212.5	382.5	60	882	3.83	0.261
		50	735	3.96	0.269
		40	588	4.10	0.279
		30	441	4.25	0.289
		20	294	4.42	0.301
		10	147	4.61	0.314
		4.3662	64.18	4.73	0.322
225	405	60	882	4.52	0.308
		50	735	4.71	0.320
		40	588	4.92	0.335
		30	441	5.66	0.351
		20	294	5.43	0.369
		10	147	5.75	0.391
		6.8601	100.84	5.86	0.399
237.5	427.5	60	882	6.12	0.416
		50	735	6.46	0.440
		40	588	6.86	0.467
		30	441	7.34	0.499
		20	294	7.92	0.539
		10.312	151.59	8.62	0.587
250	450	60	882	8.34	0.568
		50	735	9.05	0.616
		40	588	9.95	0.677
		30	441	11.1	0.755
		20	294	12.8	0.871
		14.891	218.90	14.0	0.953
262.5	472.5	60	882	11.9	0.810
		50	735	13.5	0.919
		40	588	15.9	1.08
		30	441	19.7	1.34
		20.795	305.69	27.4	1.86
273.16	491.67	60	882	18.2	1.24
		50	735	21.9	1.49
		40	588	28.7	1.95
		30	441	49.6	3.38
		27.022	397.22	73.3	4.99

TABLE 2.4

COMPRESSIBILITY, Z = PV/RT, OF REAL GAS DIBORANE (REF. 2.16)

P(Atm.)	0.01	0.1	0.4	0.7	1	4	7	10	40	70	100
T(°K)											
130	0.9986										
140	0.9990										
150	0.9992										
160	0.9994	0.9935									
170	0.9995	0.9948	0.9787								
180	0.9996	0.9958	0.9828	0.9695							
190	0.9996	0.9965	0.9858	0.9749	0.9638						
200	0.9997	0.9971	0.9882	0.9791	0.9699						
210	0.9998	0.9975	0.9900	0.9824	0.9747	0.8905					
220	0.9998	0.9979	0.9915	0.9850	0.9785	0.9082					
230	0.9998	0.9982	0.9927	0.9871	0.9815	0.9221	0.8547				
240	0.9998	0.9984	0.9936	0.9888	0.9840	0.9331	0.8768	0.8128			
250	0.9999	0.9986	0.9944	0.9902	0.9860	0.9420	0.8941	0.8413			
260	0.9999	0.9988	0.9951	0.9914	0.9877	0.9493	0.9081	0.8636			
270	0.9999	0.9989	0.9957	0.9924	0.9891	0.9553	0.9196	0.8815			
280	0.9999	0.9990	0.9961	0.9932	0.9903	0.9604	0.9291	0.8961			
290	0.9999	0.9991	0.9966	0.9940	0.9914	0.9648	0.9371	0.9082			
300	0.9999	0.9992	0.9969	0.9946	0.9922	0.9685	0.9439	0.9185	0.5595	0.3164	0.4165
310	0.9999	0.9993	0.9972	0.9951	0.9930	0.9717	0.9498	0.9272	0.6403	0.3521	0.4322
320	0.9999	0.9994	0.9975	0.9956	0.9937	0.9745	0.9549	0.9347	0.6945	0.4166	0.4507
330	0.9999	0.9994	0.9977	0.9960	0.9943	0.9770	0.9593	0.9412	0.7354	0.4994	0.4748
340	0.9999	0.9995	0.9979	0.9964	0.9948	0.9791	0.9632	0.9470	0.7679	0.5722	0.5073
350	1.0000	0.9995	0.9981	0.9967	0.9953	0.9810	0.9666	0.9520	0.7947	0.6304	0.5478
360	1.0000	0.9996	0.9983	0.9970	0.9957	0.9828	0.9697	0.9565	0.8173	0.6771	0.5918
370	1.0000	0.9996	0.9984	0.9973	0.9961	0.9843	0.9724	0.9604	0.8366	0.7157	0.6345
380	1.0000	0.9996	0.9986	0.9975	0.9964	0.9857	0.9749	0.9640	0.8533	0.7480	0.6736
390	1.0000	0.9997	0.9987	0.9977	0.9967	0.9869	0.9771	0.9672	0.8680	0.7755	0.7085
400	1.0000	0.9997	0.9988	0.9979	0.9970	0.9881	0.9791	0.9701	0.8807	0.7994	0.7394
410	1.0000	0.9997	0.9989	0.9980	0.9973	0.9891	0.9809	0.9727	0.8924	0.8202	0.7667
420	1.0000	0.9997	0.9990	0.9983	0.9975	0.9900	0.9826	0.9751	0.9027	0.8386	0.7910
430	1.0000	0.9998	0.9991	0.9984	0.9977	0.9909	0.9841	0.9773	0.9119	0.8550	0.8127
440	1.0000	0.9998	0.9992	0.9985	0.9979	0.9917	0.9855	0.9793	0.9203	0.8696	0.8321
450	1.0000	0.9998	0.9992	0.9987	0.9981	0.9924	0.9867	0.9811	0.9278	0.8827	0.8495
460	1.0000	0.9998	0.9993	0.9988	0.9983	0.9931	0.9879	0.9828	0.9347	0.8945	0.8653
470	1.0000	0.9998	0.9994	0.9989	0.9984	0.9937	0.9890	0.9843	0.9410	0.9053	0.8796
480	1.0000	0.9999	0.9994	0.9990	0.9986	0.9942	0.9900	0.9857	0.9467	0.9150	0.8926
490	1.0000	0.9999	0.9995	0.9991	0.9987	0.9948	0.9909	0.9871	0.9520	0.9240	0.9044
500	1.0000	0.9999	0.9995	0.9992	0.9988	0.9952	0.9917	0.9883	0.9568	0.9321	0.9153
510	1.0000	0.9999	0.9996	0.9992	0.9989	0.9957	0.9925	0.9894	0.9613	0.9396	0.9252
520	1.0000	0.9999	0.9996	0.9993	0.9990	0.9961	0.9933	0.9905	0.9654	0.9465	0.9344
530	1.0000	0.9999	0.9996	0.9994	0.9991	0.9965	0.9940	0.9914	0.9692	0.9529	0.9428
540	1.0000	0.9999	0.9997	0.9994	0.9992	0.9969	0.9946	0.9723	0.9728	0.9588	0.9506
550	1.0000	0.9999	0.9997	0.9995	0.9993	0.9972	0.9952	0.9932	0.9761	0.9642	0.9578
560	1.0000	0.9999	0.9997	0.9996	0.9994	0.9975	0.9957	0.9940	0.9791	0.9692	0.9644
570	1.0000	0.9999	0.9998	0.9996	0.9994	0.9978	0.9963	0.9947	0.9820	0.9739	0.9706
580	1.0000	1.0000	0.9998	0.9997	0.9995	0.9981	0.9967	0.9954	0.9846	0.9783	0.9764
590	1.0000	1.0000	0.9998	0.9997	0.9996	0.9984	0.9972	0.9961	0.9871	0.9823	0.9817
600	1.0000	1.0000	0.9999	0.9998	0.9996	0.9986	0.9976	0.9967	0.9894	0.9861	0.9867

TABLE 2.4

(Concluded)

P(Atm.) T(°K)	0.01	0.1	0.4	0.7	1	4	7	10	40	70	100
610	1.0000	1.0000	0.9999	0.9998	0.9997	0.9988	0.9980	0.9972	0.9915	0.9896	0.9914
620	1.0000	1.0000	0.9999	0.9998	0.9998	0.9990	0.9984	0.9978	0.9935	0.9929	0.9957
630	1.0000	1.0000	0.9999	0.9999	0.9998	0.9993	0.9987	0.9983	0.9954	0.9960	0.9998
640	1.0000	1.0000	0.9999	0.9999	0.9999	0.9994	0.9991	0.9987	0.9972	0.9989	1.0036
650	1.0000	1.0000	1.0000	0.9999	0.9999	0.9995	0.9994	0.9992	0.9989	1.0016	1.0071
660	1.0000	1.0000	1.0000	1.0000	0.9999	0.9998	0.9997	0.9996	1.0004	1.0041	1.0104
670	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	0.9999	1.0000	1.0019	1.0065	1.0036
680	1.0000	1.0000	1.0000	1.0000	1.0000	1.0001	1.0002	1.0003	1.0032	1.0087	1.0165
600	1.0000	1.0000	1.0000	1.0000	1.0000	1.0002	1.0005	1.0007	1.0045	1.0108	1.0192
700	1.0000	1.0000	1.0000	1.0000	1.0007	1.0004	1.0007	1.0010	1.0050	1.0128	1.0218
710	1.0000	1.0000	1.0000	1.0000	1.0001	1.0005	1.0009	1.0013	1.0069	1.0146	1.0243
720	1.0000	1.0000	1.0000	1.0001	1.0002	1.0006	1.0011	1.0016	1.0078	1.0164	1.0265
730	1.0000	1.0000	1.0000	1.0001	1.0002	1.0007	1.0013	1.0019	1.0090	1.0180	1.0237
740	1.0000	1.0000	1.0000	1.0001	1.0002	1.0008	1.0015	1.0021	1.0099	1.0196	1.0307
750	1.0000	1.0000	1.0001	1.0002	1.0002	1.0009	1.0017	1.0024	1.0108	1.0210	1.0326
760	1.0000	1.0000	1.0001	1.0002	1.0003	1.0010	1.0018	1.0026	1.0017	1.0224	1.0344
770	1.0000	1.0000	1.0001	1.0002	1.0003	1.0011	1.0020	1.0028	1.0125	1.0237	1.0361
780	1.0000	1.0000	1.0001	1.0002	1.0003	1.0011	1.0021	1.0030	1.0133	1.0249	1.0377
790	1.0000	1.0000	1.0001	1.0002	1.0003	1.0013	1.0022	1.0032	1.0140	1.0260	1.0392
800	1.0000	1.0000	1.0001	1.0002	1.0003	1.0013	1.0024	1.0034	1.0146	1.0271	1.0406
850	1.0000	1.0000	1.0002	1.0003	1.0004	1.0017	1.0029	1.0042	1.0175	1.0317	1.0466
900	1.0000	1.0000	1.0002	1.0003	1.0005	1.0019	1.0053	1.0048	1.0196	1.0351	1.0510
950	1.0000	1.0001	1.0002	1.0004	1.0005	1.0021	1.0037	1.0052	1.0213	1.0377	1.0543
1000	1.0000	1.0001	1.0002	1.0004	1.0006	1.0022	1.0039	1.0056	1.0025	1.0396	1.0567
1050	1.0000	1.0001	1.0002	1.0004	1.0006	1.0023	1.0041	1.0068	1.0233	1.0409	1.0585
1100	1.0000	1.0001	1.0002	1.0004	1.0006	1.0024	1.0042	1.0060	1.0240	1.0419	1.0597
1150	1.0000	1.0001	1.0002	1.0004	1.0006	1.0025	1.0043	1.0061	1.0244	1.0426	1.0606
1200	1.0000	1.0001	1.0003	1.0004	1.0006	1.0025	1.0044	1.0062	1.0447	1.0430	1.0611
1250	1.0000	1.0001	1.0003	1.0004	1.0006	1.0025	1.0044	1.0063	1.0249	1.0432	1.0613
1300	1.0000	1.0001	1.0003	1.0004	1.0006	1.0025	1.0044	1.0063	1.0250	1.0433	1.0614
1350	1.0000	1.0001	1.0003	1.0004	1.0006	1.0025	1.0044	1.0063	1.0250	1.0433	1.0613
1400	1.0000	1.0001	1.0003	1.0004	1.0006	1.0025	1.0044	1.0063	1.0250	1.0432	1.0610
1450	1.0000	1.0001	1.0003	1.0004	1.0006	1.0025	1.0044	1.0063	1.0248	1.0429	1.0607
1500	1.0000	1.0001	1.0003	1.0004	1.0006	1.0025	1.0044	1.0062	1.0246	1.0427	1.0604
273.16	0.9999	0.9990	0.9958	0.9927	0.9895	0.9570	0.9228	0.8864			
298.16	0.9999	0.9992	0.9968	0.9945	0.9921	0.9678	0.9428	0.9167	0.5387	0.3116	0.4137

TABLE 2.5

DENSITY RATIO, ρ/ρ_0* OF REAL GAS DIBORANE (REF. 2.16)

P(Atm.)	0.01	0.1	0.4	0.7	1	4	7	10	40	70	100
T(°K)											
130	.020820										
140	.019327										
150	.018034										
160	.016904	.17004									
170	.015907	.15983	.64975								
180	.015022	.15081	.61118	1.0842							
190	.014230	.14276	.57724	1.0215	1.4761						
200	.013518	.13555	.54706	.96621	1.3934						
210	.012874	.12902	.52005	.91713	1.3206	5.7815					
220	.012288	.12311	.49567	.87313	1.2557	5.4111					
230	.011754	.11773	.47356	.83339	1.1974	5.0983	9.6249				
240	.011264	.11280	.45338	.79728	1.1446	4.8283	8.9919	13.857			
250	.010813	.10827	.43490	.76430	1.0966	4.5913	8.4643	12.851			
260	.010397	.10409	.41789	.73403	1.0526	4.3807	8.0134	12.038			
270	.010012	.10022	.40218	.70614	1.0121	4.1920	7.6205	11.357			
280	.0096535	.096628	.38763	.68034	.97479	4.0208	7.2731	10.773			
290	.0093206	.093286	.37411	.65641	.94019	3.8646	6.9622	10.262			
300	.0090099	.090169	.36151	.63414	.90805	3.7212	6.6814	9.8093	64.403	199.33	216.33
310	.0087193	.087253	.34975	.61335	.87807	3.5892	6.4261	9.4036	54.467	173.36	201.72
320	.0084468	.084521	.33872	.59390	.85005	3.4671	5.7582	9.0365	48.644	141.94	187.43
330	.0081908	.081955	.32838	.57566	.82379	3.3536	5.9769	8.7020	44.555	114.80	172.50
340	.0079499	.079540	.31866	.55852	.79914	3.2478	5.7777	8.3951	41.411	97.252	156.70
350	.0077228	.077264	.30949	.54238	.77594	3.1488	5.5926	8.1122	38.870	85.759	140.97
360	.0075083	.075115	.30085	.55072	.75407	3.0563	5.4201	7.8500	36.747	77.617	126.86
370	.0073053	.073082	.29267	.51278	.73341	2.9690	5.2588	7.6063	34.929	71.450	115.13
380	.0071131	.071157	.28493	.49917	.71386	2.8868	5.1076	7.3787	33.343	66.567	105.60
390	.0069307	.069330	.27759	.48626	.69534	2.8092	4.9653	7.1657	31.939	62.557	97.828
400	.0067574	.067591	.27062	.47401	.67777	2.7357	4.8314	6.9661	30.684	59.172	91.397
410	.0065926	.065942	.26399	.46237	.66107	2.6662	4.7048	6.7778	29.550	56.262	85.996
420	.0064357	.064366	.25768	.45129	.64518	2.6002	4.5850	6.6002	28.518	53.718	81.361
430	.0062860	.062869	.25167	.44078	.63004	2.5376	4.4715	6.4323	27.572	51.466	77.350
440	.0061431	.061439	.24593	.43065	.61560	2.4779	4.3637	6.2733	26.702	49.452	73.829
450	.0060066	.060075	.24044	.42100	.60176	2.4211	4.2612	6.1223	25.896	47.635	70.707
460	.0058760	.058768	.23520	.41181	.58859	2.3669	4.1636	5.9790	25.146	45.983	67.910
470	.0057510	.057517	.23018	.40300	.57598	2.3151	4.0706	5.8426	24.447	44.470	65.385
480	.0056312	.056319	.22537	.39457	.56390	2.2655	3.9818	5.7126	23.793	43.079	63.091
490	.0055163	.055169	.22076	.38648	.55233	2.2181	3.8969	5.5886	23.178	41.792	60.994
500	.0054060	.054065	.21632	.37872	.54122	2.1727	3.8157	5.4701	22.600	40.598	59.065
510	.0052999	.053004	.21207	.37127	.53085	2.1291	3.7379	5.3567	22.053	39.484	57.284
520	.0051980	.051980	.20799	.36410	.52029	2.0873	3.6633	5.2481	21.537	38.442	55.633
530	.0051000	.051000	.20406	.35721	.51043	2.0471	3.5917	5.1440	21.047	37.465	54.095
540	.0050055	.050055	.20027	.35057	.50093	2.0085	3.5229	5.0441	20.582	36.546	52.658
550	.0049145	.049145	.19663	.34415	.49178	1.9713	3.4568	4.9482	20.140	35.679	51.312
560	.0048267	.048267	.19311	.33799	.48296	1.9353	3.3932	4.8559	19.719	34.859	50.047
570	.0047421	.047421	.18972	.33205	.47446	1.9008	3.3319	4.7672	19.317	34.083	48.856
580	.0046603	.046603	.18644	.32631	.46621	1.8675	3.2729	4.6818	18.933	33.346	47.730
590	.0045813	.045813	.18328	.32077	.45828	1.8354	3.2160	4.5994	18.566	32.646	46.666
600	.0045050	.045050	.18022	.31541	.45062	1.8044	3.1607	4.5200	18.214	31.979	45.656
610	.0044311	.044311	.17726	.31023	.44322	1.7744	3.1077	4.4434	17.876	31.342	44.697
620	.0043596	.043596	.17439	.30522	.43605	1.7454	3.0565	4.3690	17.552	30.735	43.784
630	.0042904	.042904	.17162	.30036	.42911	1.7174	3.0069	4.2976	17.241	30.153	42.912
640	.0042234	.042234	.16894	.29566	.42239	1.6903	2.9590	4.2286	16.941	29.595	42.084
650	.0041584	.041584	.16634	.29109	.41584	1.6639	2.9126	4.1617	16.652	29 065	41.290

TABLE 2.5

(Concluded)

P(Atm.) T(°K)	0.01	0.1	0.4	0.7	1	4	7	10	40	70	100
660	.0040954	.040954	.16382	.28668	.40954	1.6384	2.8675	4.0968	16.376	28.550	40.531
670	.0040343	.040343	.16137	.28240	.40343	1.6137	2.8240	4.0343	16.108	28.058	39.803
680	.0039750	.039750	.15900	.27825	.39750	1.5899	2.7820	3.9739	15.849	27.584	39.105
690	.0039174	.039174	.15669	.27421	.39174	1.5666	2.7412	3.9148	15.599	27.128	38.434
700	.0038614	.038614	.15446	.27030	.38614	1.5441	2.7012	3.8576	15.357	26.688	37.789
710	.0038070	.038070	.15228	.26649	.38066	1.5222	2.6626	3.8022	15.124	26.265	37.169
720	.0037541	.037541	.15017	.26277	.37537	1.5008	2.6251	3.7483	14.898	25.856	36.571
730	.0037027	.037027	.14811	.25916	.37022	1.4801	2.5887	3.6960	14.679	25.460	35.995
740	.0036527	.036527	.14611	.25566	.36521	1.4599	2.5533	3.6452	14.467	25.078	35.439
750	.0036040	.036040	.14416	.25225	.36033	1.4403	2.5188	3.5957	14.261	24.709	34.902
760	.0035565	.035565	.14225	.24892	.35558	1.4212	2.4853	3.5473	14.062	24.351	34.383
770	.0035104	.035104	.14040	.24569	.35096	1.4027	2.4526	3.5004	13.868	24.004	33.881
780	.0034654	.034654	.13860	.24253	.34645	1.3846	2.4209	3.4548	13.680	23.669	33.396
790	.0034215	.034215	.13685	.23946	.34206	1.3669	2.3899	3.4105	13.497	23.343	32.925
800	.0033787	.033787	.13513	.23647	.33778	1.3497	2.3597	3.3672	13.320	23.027	32.470
850	.0031800	.031800	.12718	.22255	.31789	1.2700	2.2195	3.1667	12.501	21.576	30.386
900	.0030033	.030033	.12011	.21018	.30022	1.1991	2.0953	2.9890	11.782	20.311	28.577
950	.0028452	.028452	.11379	.19911	.28438	1.1358	1.9844	2.8304	11.144	19.194	26.988
1000	.0027030	.027030	.10810	.18915	.27015	1.0789	1.8847	2.6880	10.575	18.201	25.580
1050	.0025743	.025743	.10295	.18014	.25728	1.0274	1.7947	2.5594	10.062	20.163	24.322
1100	.0024572	.024572	.098271	.17195	.24558	.98065	1.7129	2.4426	9.5989	16.509	23.189
1150	.0023506	.023504	.092998	.16447	.23490	.93787	1.6383	2.3361	9.1776	15.781	22.163
1200	.0022525	.022525	.090081	.15762	.22511	.89876	1.5699	2.2386	8.7926	15.117	21.230
1250	.0021624	.021624	.086478	.15131	.21611	.86279	1.5071	2.1489	8.4395	14.509	20.376
1300	.0020792	.020792	.083152	.14549	.20780	.82960	1.4491	2.0662	8.1143	13.950	19.591
1350	.0020022	.020022	.080072	.14010	.20010	.79887	1.3954	1.9897	7.8138	13.434	18.867
1400	.0019307	.019307	.077212	.13510	.19295	.77034	1.3456	1.9186	7.5352	12.956	18.198
1450	.0018641	.018641	.074550	.13044	.18630	.74378	1.2992	1.8525	7.2761	12.512	17.576
1500	.0018020	.018020	.072065	.12609	.18009	.71900	1.2559	1.7908	7.0346	12.098	16.997
273.16	.0098960	.099051	.39747	.69777	1.0000	4.1358	7.5064	11.164			
298.16	.0090655	.090727	.36376	.63811	.91378	3.7469	6.6312	9.8893	67.316	203.66	219.15

*ρo is the density of B_2H_6 gas at 1 atm and 273.15 K. To convert ρ/ρo to density in g/cc, multiply the tabular values by 1.22835 x 10^{-3}; density in lb/cu ft can be obtained by multiplying ρ/ρo by 7.79324 x 10^{-2}

TABLE 2.6

ENTHALPY FUNCTION, $(H-E_0^0)/RT^*$, OF REAL GAS DIBORANE (REF. 2.16)

P(Atm.)	0.01	0.1	0.4	0.7	1	4	7	10	40	70	100
T(°K)											
130	4.049										
140	4.068										
150	4.090										
160	4.115	4.095									
170	4.144	4.127	4.070								
180	4.175	4.162	4.116	4.069							
190	4.210	4.199	4.162	4.124	4.085						
200	4.248	4.239	4.208	4.177	4.145						
210	4.290	4.282	4.256	4.230	4.204	3.915					
220	4.334	4.328	4.306	4.284	4.262	4.024					
230	4.382	4.377	4.358	4.340	4.321	4.122	3.894				
240	4.433	4.428	4.413	4.397	4.381	4.212	4.024	3.808			
250	4.487	4 483	4.469	4.455	4.442	4.297	4.139	3.963			
260	4.543	4.540	4.528	4.516	4.504	4.379	4.244	4.097			
270	4.602	4.599	4.589	4.578	4.568	4.459	4.342	4.217			
280	4.664	4.661	4.652	4.643	4.633	4.537	4.436	4.328			
290	4.728	4.725	4.717	4.709	4.700	4.615	4.526	4.432			
300	4.794	4.791	4.784	4.777	4.769	4.693	4.614	4.531	3.245	1.273	1.059
310	4.861	4.859	4.853	4.846	4.839	4.771	4.700	4.626	3.612	1.850	1.549
320	4.931	4.929	4.923	4.917	4.911	4.849	4.864	4.719	3.872	2.437	1.958
330	5.002	5.000	4.995	4.989	4.984	4.928	4.870	4.810	4.083	2.973	2.333
340	5.074	5.073	5.068	5.063	5.058	5.006	4.954	4.900	4.264	3.383	2.695
350	5.148	5.147	5.142	5.138	5.133	5.086	5.038	4.989	4.424	3.699	3.043
360	5.223	5.222	5.218	5.171	5.209	5.166	5.122	5.077	4.571	3.956	3.363
370	5.229	5.228	5.224	5.220	5.216	5.176	5.136	5.094	4.638	4.105	3.579
380	5.376	5.375	5.372	5.368	5.364	5.327	5.290	5.251	4.837	4.367	3.902
390	5.454	5.453	5.450	5.446	5.443	5.408	5.374	5.338	4.959	4.541	4.128
400	5.533	5.532	5.529	5.526	5.522	5.490	5.458	5.425	5.077	4.700	4.330
410	5.612	5.611	5.608	5.605	5.602	5.572	5.542	5.511	5.190	4.849	4.516
420	5.692	5.691	5.688	5.685	5.683	5.654	5.626	5.598	5.300	4.989	4.687
430	5.772	5.771	5.769	5.766	5.763	5.737	5.710	5.684	5.407	5.123	4.846
440	5.853	5.852	5.849	5.847	5.845	5.820	5.795	5.770	5.512	5.250	4.997
450	5.934	5.933	5.931	5.928	5.926	5.903	5.879	5.856	5.615	5.373	5.140
460	6.015	6.014	6.012	6.010	6.008	5.986	5.963	5.941	5.717	5.491	5.276
470	6.096	6.096	6.094	6.091	6.089	6.069	6.048	6.027	5.816	5.607	5.407
480	6.178	6.177	6.175	6.173	6.171	6.152	6.132	6.112	5.914	5.719	5.533
490	6.259	6.259	6.257	6.255	6.253	6.235	6.216	6.198	6.011	5.828	5.655
500	6.341	6.341	6.339	6.337	6.335	6.318	6.300	6.283	6.107	5.935	5.773
510	6.423	6.422	6.421	6.419	6.417	6.401	6.384	6.367	6.202	6.041	5.889
520	6.505	6.504	6.503	6.501	6.499	6.483	6.468	6.452	6.295	6.144	6.001
530	6.586	6.586	6.584	6.583	6.581	6.566	6.551	6.536	6.388	6.245	6.111
540	6.668	6.667	6.666	6.664	6.663	6.649	6.634	6.620	6.480	6.345	6.219
550	6.749	6.749	6.747	6.746	6.745	6.731	6.717	6.704	6.571	6.444	6.325
560	6.830	6.830	6.829	6.827	6.826	6.813	6.800	6.787	6.661	6.541	6.429
570	6.911	6.911	6.910	6.909	6.907	6.895	6.883	6.870	6.751	6.637	6.531
580	6.992	6.992	6.991	6.990	6.988	6.977	6.965	6.953	6.839	6.732	6.631
590	7.073	7.072	7.071	7.070	7.069	7.058	7.047	7.036	6.928	6.825	6.730
600	7.153	7.153	7.152	7.151	7.150	7.139	7.128	7.118	7.015	6.918	6.827
610	7.233	7.233	7.232	7.231	7.230	7.220	7.210	7.199	7.101	7.009	6.924
620	7.313	7.313	7.312	7.311	7.310	7.300	7.290	7.281	7.187	7.100	7.018
630	7.392	7.392	7.391	7.390	7.389	7.380	7.371	7.362	7.273	7.189	7.112
640	7.472	7.471	7.470	7.469	7.469	7.460	7.450	7.442	7.357	7.278	7.205
650	7.550	7.550	7.549	7.548	7.548	7.539	7.531	7.522	7.441	7.365	7.295

TABLE 2.6

(Concluded)

P(Atm.)	0.01	0.1	0.4	0.7	1	4	7	10	40	70	100
T(°K)											
660	7.629	7.628	7.628	7.627	7.626	7.618	7.610	7.602	7.525	7.453	7.386
670	7.707	7.707	7.706	7.705	7.704	7.696	7.689	7.681	7.607	7.539	7.476
680	7.784	7.784	7.783	7.783	7.782	7.775	7.767	7.760	7.690	7.624	7.564
690	7.862	7 862	7.861	7.860	7.859	7.852	7.845	7.838	7.771	7.709	7.651
700	7.939	7.938	7.938	7.937	7.936	7.930	7.923	7.916	7.852	7.793	7.738
710	8.015	8.015	8.014	8.014	8.013	8.006	8.000	7.994	7.932	7.876	7.823
720	8.091	8.091	8.090	8.090	8.089	8.083	8.077	8.071	8.012	7.958	7.908
730	8.167	8.167	8.166	8.165	8.165	8.159	8.153	8.147	8.091	8.039	7.992
740	8.242	8.242	8.241	8.241	8.240	8.234	8.229	8.223	8.170	8.120	8.075
750	8.317	8.316	8.316	8.315	8.315	8.309	8.304	8.299	8.247	8.200	8.157
760	8.391	8.391	8.390	8.390	8.389	8.384	8.379	8.374	8.325	8.280	8.238
770	8.465	8.465	8.464	8.464	8.463	8.458	8.453	8.448	8.401	8.358	8.319
780	8.538	8.538	8.537	8.537	8.537	8.532	8.527	8.522	8.478	8.436	8.398
790	8.611	8.611	8.610	8.610	8.609	8.605	8.600	8.596	8.553	8.514	8.477
800	8.683	8.683	8.683	8.682	8.682	8.678	8.673	8.669	8.628	8.590	8.556
850	9.038	9.038	9.038	9.038	9.037	9.034	9.030	9.027	8.994	8.964	8.937
900	9.381	9.381	9.381	9.381	9.380	9.377	9.375	9.372	9.346	9.322	9.300
950	9.712	9.712	9.712	9.711	9.711	9.709	9.707	9.704	9.684	9.665	9.648
1000	10.030	10.030	10.030	10.030	10.030	10.028	10.026	10.024	10.008	9.993	9.980
1050	10.337	10.336	10.336	10.336	10.336	10.335	10.333	10.332	10.319	10.150	10.298
1100	10.631	10.631	10.631	10.631	10.631	10.630	10.629	10.628	10.618	10.610	10.603
1150	10.914	10.914	10.914	10.914	10.914	10.913	10.912	10.911	10.905	10.899	10.894
1200	11.186	11.186	11.186	11.186	11.186	11.186	11.185	11.184	11.179	11.176	11.173
1250	11.447	11.447	11.447	11.447	11.447	11.446	11.446	11.446	11.443	11.441	11.440
1300	11.697	11.697	11.697	11.697	11.697	11.697	11.697	11.697	11.696	11.696	11.696
1350	11.938	11.938	11.938	11.938	11.938	11.938	11.938	11.938	11.939	11.940	11.941
1400	12.169	12.169	12.169	12.169	12.169	12.170	12.170	12.170	12.172	12.174	12.176
1450	12.392	12.392	12.392	12.392	12.392	12.392	12.392	12.392	12.395	12.398	12.401
1500	12.605	12.605	12.605	12.605	12.605	12.606	12.606	12.606	12.610	12.614	12.618
273.16	4.622	4.619	4.609	4.598	4.588	4.484	4.372	4.253			
298.16	4.781	4.779	4.772	4.764	4.756	4.679	4.598	4.513	3.152	1.159	0.953

* To convert $(H-E_0^0)/RT$ to $(H-E_0^0)/T$ in units of cal/g-K or Btu/lb-K, multiply the tabular values by 7.7708×10^{-2}.

TABLE 2.7

FREE ENERGY FUNCTION, $-(F-E_o^o)/RT^*$, OF REAL GAS DIBORANE (REF. 2.16)

P(Atm)	0.01	0.1	0.4	0.7	1	4	7	10	40	70	100
T(°K)											
130	24.128										
140	24.428										
150	24.709										
160	24.974	22.684									
170	25.224	22.932	21.579								
180	25.462	23.167	21.809	21.277							
190	25.688	23.393	22.029	21.493	21.160						
200	25.905	23.608	22.241	21.701	21.364						
210	26.113	23.816	22.446	21.903	21.563	20.360					
220	26.314	24.016	22.643	22.098	21.756	20.524					
230	26.508	24.209	22.835	22.287	21.943	20.689	20.281				
240	26.695	24.396	23.020	22.471	22.126	20.854	20.422	20.212			
250	26.877	24.578	23.201	22.651	22.303	21.017	20.567	20.332			
260	27.054	24.754	23.376	22.825	22.477	21.179	20.714	20.462			
270	27.227	24.927	23.548	22.996	22.647	21.339	20.863	20.596			
280	27.395	25.095	23.715	23.162	22.813	21.496	21.011	20.733			
290	27.560	25.259	23.879	23.326	22.975	21.652	21.158	20.871			
300	27.721	25.421	24.040	23.486	23.135	21.805	21.305	21.010	20.589	21.535	21.216
310	27.880	25.579	24.197	23.643	23.291	21.957	21.451	21.150	20.531	21.355	21.148
320	28.035	25.734	24.352	23.797	23.445	22.106	21.519	21.289	20.548	21.115	21.093
330	28.188	25.887	24.505	23.949	23.597	22.254	21.738	21.427	20.598	20.903	21.037
340	28.338	26.037	24.655	24.099	23.746	22.399	21.880	21.565	20.669	20.792	20.974
350	28.486	26.185	24.802	24.246	23.893	22.543	22.021	21.702	20.751	20.753	20.911
360	28.633	26.331	24.948	24.435	24.038	22.686	22.160	21.839	20.842	20.759	20.865
370	28.847	26.545	25.162	24.605	24.252	22.897	22.368	22.044	21.010	20.861	20.913
380	28.919	26.617	25.234	24.677	24.323	22.966	22.435	22.108	21.042	20.843	20.845
390	29.052	26.750	25.366	24.809	24.455	23.096	22.563	22.234	21.139	20.900	20.860
400	29.199	26.897	25.513	24.956	24.602	23.240	22.706	22.374	21.255	20.982	20.907
410	29.336	27.034	25.651	25.093	24.739	23.376	22.839	22.506	21.365	21.064	20.959
420	29.473	27.171	25.786	25.229	24.874	23.510	22.972	22.637	21.476	21.151	21.021
430	29.607	27.305	25.921	25.364	25.009	23.643	23.103	22.767	21.589	21.242	21.091
440	29.741	27.439	26.055	25.497	25.142	23.774	23.234	22.896	21.702	21.337	21.168
450	29.873	27.571	26.187	25.629	25.274	23.905	23.363	23.024	21.816	21.435	21.249
460	30.005	27.703	26.318	25.760	25.405	24.035	23.492	23.152	21.931	21.535	21.335
470	30.135	27.833	26.448	25.890	25.535	24.164	23.620	23.278	22.046	21.637	21.424
480	30.264	27.962	26.577	26.019	25.664	24.292	23.746	23.404	22.161	21.741	21.516
490	30.392	28.090	26.705	26.147	25.792	24.419	23.873	23.529	22.276	21.846	21.610
500	30.520	28.217	26.832	26.274	25.919	24.545	23.998	23.654	22.391	21.951	21.707
510	30.646	28.344	26.959	26.400	26.045	24.670	24.122	23.777	22.507	22.058	21.805
520	30.772	28.469	27.084	26.526	26.170	24.795	24.246	23.900	22.622	22.165	21.905
530	30.896	28.594	27.209	26.650	26.294	24.919	24.369	24.023	22.737	22.273	22.005
540	31.020	28.718	27.332	26.774	26.418	25.042	24.492	24.145	22.852	22.382	22.107
550	31.143	28.841	27.455	26.897	26.541	25.164	24.613	24.266	22.967	22.490	22.210
560	31.266	28.963	27.578	27.019	26.663	25.285	24.734	24.386	23.082	22.599	22.313
570	31.387	29.085	27.699	27.140	26.785	25.406	24.855	24.506	23.196	22.708	22.417
580	31.508	29.206	27.820	27.261	26.905	25.526	24.974	24.625	23.310	22.817	22.522
590	31.628	29.326	27.940	27.381	27.025	25.646	25.094	24.744	23.424	22.927	22.627
600	31.748	29.445	28.060	27.501	27.145	25.765	25.212	24.862	23.538	23.036	22.732

TABLE 2.7

(Concluded)

P(Atm.) T(°K)	0.01	0.1	0.4	0.7	1	4	7	10	40	70	100
610	31.867	29.564	28.179	27.620	27.264	25.883	25.330	24.979	23.651	23.145	22.837
620	31.985	29.683	28.297	27.738	27.382	26.001	25.447	25.096	23.764	23.255	22.943
630	32.103	29.800	28.414	27.855	27.499	26.118	25.564	25.213	23.877	23.364	23.049
640	32.220	29.917	28.531	27.972	27.616	26.235	25.680	25.329	23.989	23.473	23.155
650	32.336	30.034	28.648	28.089	27.732	26.351	25.796	25.444	24.102	23.582	23.261
660	32.452	30.150	28.764	28.204	27.848	26.466	25.911	25.559	24.213	23.691	23.367
670	32.567	30.265	28.879	28.320	27.963	26.581	26.026	25.673	24.325	23.799	23.473
680	32.682	30.380	28.994	28.434	28.078	26.696	26.140	25.787	24.436	23.908	23.579
690	32.796	30.494	29.108	28.549	28.192	26.810	26.253	25.900	24.547	24.016	23.685
700	32.910	30.607	29.222	28.662	28.306	26.923	26.366	26.013	24.657	24.124	23.791
710	33.023	30.721	29.335	28.775	28.419	27.036	26.479	26.125	24.767	24.232	23.897
720	33.136	30.833	29.447	28.888	28.532	27.148	26.591	26.237	24.877	24.340	24.003
730	33.248	30.945	29.559	29.000	28.644	27.260	26.703	26.349	24.986	24.447	24.108
740	33.359	31.057	29.671	29.112	28.755	27.371	26.814	26.460	25.095	24.554	24.214
750	33.471	31.168	29.782	29.223	28.866	27.482	26.925	26.570	25.203	24.661	24.319
760	33.581	31.279	29.893	29.333	28.977	27.592	27.035	26.680	25.312	24.767	24.424
770	33.691	31.389	30.003	29.443	29.087	27.702	27.145	26.790	25.420	24.874	24.529
780	33.801	31.499	30.112	29.553	29.197	27.812	27.254	26.899	25.527	24.980	24.633
790	33.910	31.608	30.222	29.662	29.306	27.921	27.363	27.007	25.634	25.085	24.738
800	34.019	31.717	30.330	29.771	29.414	28.029	27.471	27.116	25.741	25.191	24.842
850	34.556	32.254	30.868	30.308	29.951	28.566	28.007	27.651	26.270	25.714	25.359
900	35.083	32.780	31.394	30.834	30.478	29.091	28.532	28.175	26.789	26.228	25.870
950	35.599	33.296	31.910	31.350	30.994	29.607	29.047	28.690	27.300	26.735	26.373
1000	36.105	33.803	32.416	31.857	31.500	30.113	29.552	29.195	27.802	27.234	26.870
1050	36.602	34.299	32.913	32.353	31.996	30.609	30.049	29.691	28.295	27.876	27.358
1100	37.090	34.787	33.401	32.841	32.484	31.097	30.536	30.178	28.780	28.208	27.839
1150	37.569	35.266	33.879	33.320	32.963	31.575	31.014	30.656	29.256	28.683	28.313
1200	38.039	35.736	34.350	33.790	33.433	32.045	31.484	31.126	29.725	29.150	28.779
1250	38.501	36.198	34.312	34.252	33.895	32.507	31.946	31.588	30.185	29.610	29.237
1300	38.955	36.652	35.266	34.706	34.349	32.961	32.399	32.041	30.638	30.061	29.688
1350	39.401	37.098	35.712	35.152	34.795	33.407	32.845	32.487	31.083	30.506	30.132
1400	39.839	37.536	36.150	35.590	35.233	33.845	33.284	32.925	31.520	30.943	30.568
1450	40.270	37.967	36.581	36.021	35.664	34.276	33.714	33.356	31.951	31.372	30.998
1500	40.694	38.391	37.005	36.445	36.088	34.700	34.138	33.779	32.374	31.795	31.420
273.16	27.281	24.980	23.601	23.049	22.699	21.389	20.909	20.639			
298.16	27.692	25.391	24.010	23.457	23.106	21.777	21.278	20.985	20.619	21.564	21.231

* To convert $-(F-E_0^0)/RT$ to $-(F-E_0^0)/T$ in units of cal/g-K or Btu/lb-K, multiply the tabular values by 7.17708×10^{-2}.

TABLE 2.8

ENTROPY, S/R*, OF REAL GAS DIBORANE (REF. 2.16)

P(Atm.)	0.01	0.1	0.4	0.7	1	4	7	10	40	70	100
T(°K)											
130	28.177										
140	28.496										
150	28.800										
160	29.089	26.778									
170	29.368	27.058	25.649								
180	29.637	27.329	25.924	25.346							
190	29.898	27.592	26.191	25.616	25.244						
200	30.153	27.847	26.450	25.878	25.509						
210	30.403	28.098	26.702	26.133	25.767	24.275					
220	30.648	28.343	26.950	26.382	26.018	24.548					
230	30.890	28.585	27.193	26.627	26.264	24.811	24.175				
240	31.128	28.824	27.433	26.868	26.506	25.066	24.446	24.020			
250	31.364	29.060	27.670	27.106	26.745	25.314	24.706	24.295			
260	31.598	29.294	27.904	27.341	26.981	25.558	24.959	24.559			
270	31.829	29.526	28.137	27.574	27.214	25.797	25.205	24.813			
280	32.059	29.756	28.367	27.805	27.446	26.034	25.447	25.061			
290	32.288	29.985	28.596	28.034	27.676	26.267	25.684	25.303			
300	32.515	30.212	28.824	28.262	27.904	26.498	25.919	25.541	23.834	22.807	22.275
310	32.741	30.438	29.050	28.489	28.131	26.728	26.151	25.776	24.143	23.205	22.698
320	32.966	30.663	29.275	28.714	28.356	26.955	26.383	26.008	24.420	23.552	23.051
330	33.190	30.887	29.499	28.938	28.580	27.181	26.608	26.238	24.681	23.876	23.370
340	33.413	31.110	29.722	29.162	28.804	27.406	26.834	26.465	24.932	24.175	23.669
350	33.635	31.332	29.945	29.384	29.026	27.629	27.059	26.691	25.176	24.452	23.954
360	33.856	31.553	30.166	29.605	29.248	27.852	27.282	26.915	25.414	24.714	24.228
370	34.076	31.773	30.386	29.826	29.468	28.073	27.504	27.138	25.648	24.966	24.492
380	34.296	31.993	30.606	30.045	29.688	28.293	27.725	27.360	25.878	25.210	24.748
390	34.506	32.203	30.816	30.256	29.898	28.504	27.937	27.572	26.098	25.441	24.988
400	34.732	32.429	31.042	30.482	30.124	28.730	28.163	27.799	26.332	25.683	25.238
410	34.948	32.646	31.259	30.698	30.341	28.948	28.381	28.017	26.555	25.913	25.475
420	35.164	32.862	31.475	30.914	30.557	29.164	28.598	28.234	26.776	26.140	25.708
430	35.380	33.077	31.690	31.130	30.772	29.380	28.814	28.450	26.996	26.365	25.938
440	35.594	33.291	31.904	31.344	30.987	29.594	29.028	28.666	27.215	26.587	26.165
450	35.807	33.504	32.117	31.557	31.200	29.808	29.242	28.880	27.432	26.808	26.389
460	36.020	33.717	32.330	31.770	31.413	30.021	29.455	29.093	27.647	27.027	26.611
470	36.231	33.928	32.542	31.981	31.624	30.232	29.667	29.305	27.862	27.244	26.831
480	36.442	34.139	32.752	32.192	31.835	30.443	29.878	29.516	28.075	27.460	27.049
490	36.652	34.349	32.962	32.402	32.045	30.654	30.089	29.727	28.287	27.674	27.265
500	36.861	34.558	33.171	32.611	32.254	30.863	30.298	29.936	28.498	27.887	27.480
510	37.069	34.766	33.379	32.819	32.462	31.071	30.506	30.145	28.708	28.099	27.694
520	37.276	34.973	33.587	33.027	32.669	31.278	30.714	30.352	28.917	28.309	27.906
530	37.482	35.180	33.793	33.233	32.876	31.485	30.920	30.559	29.125	28.519	28.117
540	37.688	35.385	33.998	33.438	33.081	31.690	31.126	30.765	29.332	28.727	28.326
550	37.892	35.590	34.203	33.643	33.286	31.895	31.331	30.970	29.538	28.934	28.535
560	38.096	35.793	34.406	33.846	33.489	32.099	31.535	31.173	29.743	29.140	28.742
570	38.299	35.996	34.609	34.049	33.692	32.301	31.737	31.376	29.947	29.345	28.948
580	38.500	36.198	34.811	34.251	33.894	32.503	31.939	31.578	30.150	29.549	29.153
590	38.701	36.398	35.012	34.452	34.095	32.704	32.140	31.779	30.352	29.752	29.357
600	38.901	36.598	35.212	34.652	34.294	32.904	32.340	31.980	30.553	29.954	29.559

TABLE 2.8

(Concluded)

P(Atm.) T(°K)	0.01	0.1	0.4	0.7	1	4	7	10	40	70	100
610	39.100	36.797	35.410	34.850	34.493	33.103	32.539	32.179	30.753	30.155	29.761
620	39.298	36.995	35.609	35.049	34.691	33.301	32.738	32.377	30.952	30.354	29.962
630	39.495	37.192	35.806	35.246	34.889	33.498	32.935	32.574	31.150	30.553	30.161
640	39.691	37.388	36.002	35.442	35.085	33.695	33.131	32.771	31.347	30.751	30.360
650	39.886	37.584	36.197	35.637	35.280	33.890	33.327	32.966	31.543	30.948	30.557
660	40.081	37.778	36.391	35.831	35.474	34.084	33.521	33.161	31.738	31.143	30.753
670	40.274	37.971	36.585	36.025	35.668	34.278	33.715	33.354	31.932	31.338	30.949
680	40.467	38.162	36.777	36.217	35.860	34.470	33.907	33.547	32.125	31.532	31.143
690	40.658	38.355	36.969	36.409	36.052	34.662	34.099	33.739	32.318	31.725	31.337
700	40.849	38.546	37.159	36.599	36.242	34.852	34.289	33.929	32.509	31.917	31.529
710	41.038	38.735	37.349	36.789	36.432	35.042	34.479	34.119	32.699	32.107	31.720
720	41.227	38.924	37.538	36.978	36.621	35.231	34.668	34.308	32.889	32.297	31.911
730	41.415	39.112	37.725	37.165	36.808	35.419	34.856	34.496	33.077	32.486	32.100
740	41.601	39.299	37.912	37.352	36.995	35.606	35.043	34.683	33.264	32.674	32.288
750	41.787	39.485	38.098	37.538	37.181	35.791	35.229	34.869	33.451	32.861	32.476
760	41.972	39.670	38.233	37.723	37.366	35.976	35.414	35.054	33.636	33.047	32.662
770	42.156	39.854	38.467	37.907	37.550	36.161	35.598	35.238	33.821	33.232	32.847
780	42.339	40.037	38.650	38.090	37.733	36.344	35.781	35.421	34.005	33.416	33.032
790	42.521	40.219	38.832	38.272	37.915	36.526	35.963	35.603	34.187	33.599	33.215
800	42.703	40.400	39.013	38.453	38.096	36.707	36.144	35.785	34.369	33.781	33.398
850	43.595	41.292	39.905	39.346	38.989	37.599	37.037	36.677	35.264	34.677	34.296
900	44.464	42.161	40.775	40.215	39.858	38.469	37.907	37.547	36.135	35.550	35.170
950	45.311	43.008	41.621	41.062	40.705	39.316	38.754	38.394	36.983	36.400	36.021
1000	46.135	43.833	42.446	41.886	41.529	40.141	39.579	39.220	37.810	37.228	36.850
1050	46.938	44.636	43.249	42.689	42.333	40.944	40.382	40.023	38.614	38.025	37.657
1100	47.721	45.418	44.031	43.472	43.115	41.726	41.164	40.805	39.398	38.818	38.442
1150	48.482	46.180	44.793	44.233	43.877	42.488	41.926	41.568	40.161	39.582	39.207
1200	49.224	46.922	45.535	44.976	44.619	43.230	42.669	42.310	40.904	40.326	39.952
1250	49.947	47.645	46.258	45.699	45.342	43.953	43.392	43.033	41.628	41.051	40.677
1300	50.652	48.349	46.963	46.403	46.046	44.658	44.097	43.738	42.334	41.757	41.384
1350	51.339	49.036	47.650	47.090	46.733	45.345	44.784	44.425	43.021	42.445	42.073
1400	52.008	49.706	48.319	47.760	47.403	46.015	45.453	45.095	43.692	43.116	42.744
1450	52.662	50.359	48.972	48.413	48.056	46.668	46.107	45.748	44.346	43.771	43.399
1500	53.299	50.996	49.610	49.050	48.693	47.305	46.744	46.386	44.984	44.409	44.038
273.16	31.902	29.599	28.210	27.647	27.288	25.872	25.282	24.892			
298.16	32.473	30.170	28.782	28.220	27.862	26.456	25.876	25.498	23.770	22.723	22.184

* To convert S/R to S in units of cal/g-K or Btu/lb-R, multiply by 7.17708×10^{-2}.

TABLE 2.9

SPECIFIC HEAT, C_p/R^*, OF REAL GAS DIBORANE (REF. 2.16)

P(Atm.)	0.01	0.1	0.4	0.7	1	4	7	10	40	70	100
T(°K)											
130	4.283										
140	4.358										
150	4.444										
160	4.542	4.598									
170	4.652	4.696	4.853								
180	4.772	4.809	4.935	5.070							
190	4.903	4.933	5.036	5.144	5.258						
200	5.044	5.069	5.153	5.241	5.333						
210	5.194	5.215	5.285	5.357	5.431	6.369					
220	5.353	5.370	5.428	5.487	5.548	6.285					
230	5.518	5.532	5.580	5.630	5.681	6.272	7.100				
240	5.689	5.701	5.742	5.783	5.826	6.307	6.940	7.851			
250	5.866	5.876	5.911	5.945	5.981	6.378	6.876	7.539			
260	6.047	6.056	6.085	6.114	6.145	6.475	6.877	7.383			
270	6.232	6.239	6.264	6.289	6.315	6.593	6.922	7.320			
280	6.419	6.425	6.446	6.468	6.490	6.726	6.999	7.321			
290	6.608	6.613	6.632	6.650	6.669	6.871	7.101	7.366			
300	6.798	6.803	6.819	6.835	6.852	7.026	7.221	7.442	17.339	19.473	17.825
310	6.990	6.994	7.008	7.022	7.036	7.188	7.355	7.542	12.856	19.607	15.139
320	7.181	7.185	7.197	7.210	7.222	7.355	7.476	7.659	11.255	21.201	14.337
330	7.373	7.376	7.387	7.398	7.409	7.526	7.652	7.790	10.466	18.537	14.435
340	7.564	7.567	7.577	7.587	7.596	7.700	7.811	7.932	10.032	15.474	14.806
350	7.755	7.757	7.766	7.775	7.784	7.876	7.974	8.080	9.787	13.566	14.814
360	7.944	7.946	7.954	7.963	7.970	8.053	8.141	8.235	9.657	12.429	14.302
370	8.133	8.135	8.142	8.149	8.156	8.231	8.310	8.394	9.602	11.730	13.595
380	8.320	8.322	8.328	8.335	8.341	8.409	8.480	8.556	9.598	11.293	12.949
390	8.505	8.507	8.513	8.519	8.525	8.587	8.652	8.720	9.631	11.018	12.440
400	8.689	8.691	8.696	8.702	8.707	8.764	8.824	8.886	9.690	10.851	12.065
410	8.871	8.873	8.878	8.883	8.888	8.941	8.995	9.052	9.769	10.759	11.799
420	9.052	9.053	9.058	9.063	9.068	9.116	9.166	9.219	9.864	10.719	11.618
430	9.231	9.232	9.236	9.241	9.245	9.290	9.337	9.385	9.970	10.719	11.502
440	9.407	9.409	9.413	9.417	9.421	9.463	9.507	9.552	10.004	10.748	11.437
450	9.582	9.583	9.587	9.591	9.595	9.634	9.675	9.717	10.205	10.798	11.410
460	9.755	9.756	9.760	9.764	9.767	9.804	9.842	9.882	10.332	10.866	11.413
470	9.926	9.927	9.931	9.934	9.937	9.972	10.008	10.045	10.462	10.947	11.440
480	10.095	10.096	10.099	10.103	10.106	10.139	10.173	10.207	10.595	11.038	11.485
490	10.262	10.263	10.266	10.269	10.272	10.304	10.336	10.368	10.730	11.137	11.545
500	10.427	10.428	10.431	10.434	10.437	10.466	10.497	10.528	10.867	11.242	11.617
510	10.590	10.591	10.594	10.596	10.599	10.627	10.656	10.686	11.004	11.352	11.698
520	10.751	10.752	10.754	10.757	10.760	10.787	10.814	10.842	11.143	11.467	11.787
530	10.910	10.910	10.913	10.916	10.918	10.944	10.970	10.997	11.281	11.584	11.881
540	11.067	11.067	11.070	11.072	11.075	11.099	11.124	11.150	11.419	11.703	11.981
550	11.221	11.222	11.224	11.227	11.229	11.253	11.277	11.301	11.557	11.824	12.084
560	11.374	11.375	11.377	11.379	11.382	11.404	11.427	11.451	11.694	11.946	12.191
570	11.525	11.526	11.528	11.530	11.532	11.554	11.576	11.598	11.830	12.069	12.299
580	11.674	11.674	11.677	11.679	11.681	11.702	11.723	11.744	11.966	12.192	12.410
590	11.821	11.821	11.823	11.825	11.827	11.848	11.868	11.889	12.100	12.315	12.521
600	11.965	11.966	11.968	11.970	11.972	11.991	12.011	12.031	12.234	12.438	12.634
610	12.108	12.109	12.111	12.113	12.114	12.133	12.152	12.171	12.366	12.561	12.747
620	12.249	12.250	12.251	12.253	12.255	12.273	12.292	12.310	12.497	12.683	12.861
630	12.388	12.389	12.390	12.392	12.394	12.411	12.429	12.447	12.626	12.804	12.974
640	12.525	12.525	12.527	12.529	12.531	12.548	12.565	12.582	12.755	12.925	13.087
650	12.660	12.660	12.662	12.664	12.665	12.682	12.698	12.715	12.881	13.045	13.200

TABLE 2.9

(Concluded)

P(Atm.)	0.01	0.1	0.4	0.7	1	4	7	10	40	70	100
T(°K)											
660	12.793	12.793	12.795	12.797	12.798	12.814	12.830	12.846	13.007	13.164	13.313
670	12.924	12.924	12.926	12.928	12.929	12.945	12.960	12.976	13.131	13.282	13.425
680	13.053	13.054	13.055	13.057	13.058	13.073	13.088	13.103	13.253	13.399	13.536
690	13.180	13.181	13.182	13.184	13.185	13.200	13.214	13.229	13.374	13.514	13.647
700	13.306	13.306	13.308	13.309	13.311	13.325	13.339	13.353	13.493	13.629	13.756
710	13.429	13.430	13.431	13.433	13.434	13.448	13.461	13.475	13.611	13.742	13.865
720	13.551	13.551	13.553	13.554	13.555	13.569	13.582	13.595	13.727	13.853	13.972
730	13.671	13.671	13.673	13.674	13.675	13.688	13.701	13.714	13.842	13.964	14.079
740	13.789	13.789	13.790	13.792	13.793	13.806	13.818	13.831	13.955	14.073	14.184
750	13.905	13.905	13.907	13.908	13.909	13.921	13.934	13.946	14.066	14.181	14.288
760	14.019	14.020	14.021	14.022	14.023	14.035	14.047	14.059	14.176	14.287	14.391
770	14.132	14.132	14.133	14.135	14.136	14.147	14.159	14.171	14.284	14.392	14.493
780	14.243	14.243	14.244	14.245	14.247	14.258	14.269	14.280	14.391	14.495	14.593
790	14.352	14.352	14.353	14.354	14.356	14.367	14.378	14.389	14.496	14.597	14.693
800	14.459	14.460	14.461	14.462	14.463	14.474	14.484	14.495	14.599	14.698	14.791
850	14.971	14.971	14.972	14.973	14.974	14.984	14.993	15.002	15.094	15.181	15.26
900	15.442	15.443	15.444	15.444	15.445	15.454	15.462	15.471	15.552	15.628	15.69
950	15.877	15.877	15.878	15.878	15.879	15.887	15.894	15.902	15.975	16.043	16.106
1000	16.276	16.276	16.277	16.278	16.278	16.285	16.292	16.299	16.364	16.425	16.483
1050	16.643	16.644	16.644	16.645	16.645	16.652	16.658	16.664	16.723	16.800	16.830
1100	16.981	16.981	16.982	16.982	16.983	16.989	16.994	17.000	17.054	17.104	17.151
1150	17.292	17.292	17.293	17.293	17.294	17.299	17.304	17.309	17.358	17.405	17.448
1200	17.578	17.578	17.579	17.579	17.580	17.584	17.587	17.594	17.639	17.682	17.721
1250	17.841	17.842	17.842	17.842	17.843	17.847	17.852	17.856	17.898	17.937	17.974
1300	18.084	18.084	18.085	18.085	18.086	18.090	18.094	18.098	18.136	18.173	18.207
1350	18.308	18.308	18.309	18.309	18.310	18.313	18.317	18.321	18.357	18.390	18.422
1400	18.515	18.515	18.516	18.516	18.517	18.520	18.524	18.527	18.560	18.592	18.621
1450	18.707	18.707	18.707	18.708	18.708	18.711	18.714	18.718	18.749	18.778	18.806
1500	18.884	18.884	18.884	18.885	18.885	18.888	18.891	18.894	18.923	18.951	18.977
273.16	6.290	6.297	6.321	6.345	6.370	6.634	6.943	7.315			
298.16	6.763	6.768	6.784	6.801	6.818	6.997	7.198	7.426	19.245	19.994	18.692

* To convert Cp/R to C_p in units of cal/g-K or Btu/lb-R, multiply the tabular values by 7.17708x10^{-2}.

TABLE 2.10

SPECIFIC HEAT RATIO, γ, OF REAL GAS DIBORANE (REF. 2.16)

P(Atm.)	0.01	0.1	0.4	0.7	1	4	7	10	40	70	100
T(°K)											
130	1.3074										
140	1.2999										
150	1.2919										
160	1.2835	1.2901									
170	1.2748	1.2799	1.2979								
180	1.2658	1.2698	1.2837	1.2988							
190	1.2568	1.2599	1.2708	1.2824	1.2949						
200	1.2477	1.2502	1.2589	1.2680	1.2777						
210	1.2388	1.2408	1.2478	1.2551	1.2627	1.3650					
220	1.2300	1.2317	1.2374	1.2433	1.2494	1.3273					
230	1.2216	1.2230	1.2276	1.2325	1.2375	1.2984	1.3911				
240	1.2134	1.2146	1.2185	1.2225	1.2266	1.2754	1.3442	1.4505			
250	1.2057	1,2066	1.2099	1.2133	1.2167	1.2565	1.3096	1.3845			
260	1.1983	1.1991	1.2019	1.2047	1.2076	1.2406	1.2827	1.3386			
270	1.1913	1.1920	1.1944	1.1968	1.1993	1.2270	1.2611	1.3045			
280	1.1846	1.1853	1.1873	1.1894	1.1916	1.2151	1.2434	1.2780			
290	1.1784	1.1789	1.1807	1.1826	1.1844	1.2047	1.2284	1.2567			
300	1.1725	1.1730	1.1746	1.1762	1.1778	1.1954	1.2156	1.2391	2.4862	2.7355	2.5243
310	1.1670	1.1674	1.1688	1.1703	1.1717	1.1870	1.2045	1.2243	1.8713	2.6916	2.1303
320	1.1618	1.1622	1.1635	1.1647	1.1660	1.1795	1.1922	1.2117	1.6393	2.8641	1.9888
330	1.1570	1.1573	1.1584	1.1595	1.1607	1.1727	1.1860	1.2008	1.5137	2.5056	1.9715
340	1.1524	1.1527	1.1537	1.1547	1.1557	1.1665	1.1782	1.1911	1.4336	2.0959	1.9939
350	1.1481	1.1484	1.1493	1.1502	1.1511	1.1608	1.1712	1.1826	1.3778	1.8319	1.9717
360	1.1440	1.1443	1.1451	1.1460	1.1468	1.1555	1.1649	1.1750	1.3363	1.6652	1.8839
370	1.1402	1.1405	1.1412	1.1420	1.1427	1.1506	1.1591	1.1682	1.3042	1.5537	1.7718
380	1.1366	1.1369	1.1375	1.1382	1.1389	1.1461	1.1538	1.1620	1.2786	1.4749	1.6674
390	1.1333	1.1335	1.1341	1.1347	1.1354	1.1420	1.1489	1.1563	1.2576	1.4166	1.5804
400	1.1301	1.1303	1.1308	1.1314	1.1320	1.1381	1.1445	1.1512	1.2401	1.3717	1.5101
410	1.1271	1.1272	1.1278	1.1283	1.1289	1.1344	1.1403	1.1464	1.2252	1.3361	1.4535
420	1.1242	1.1244	1.1249	1.1254	1.1259	1.1310	1.1364	1.1420	1.2124	1.3073	1.4077
430	1.1215	1.1217	1.1221	1.1226	1.1231	1.1270	1.1328	1.1380	1.2012	1.2835	1.3700
440	1.1190	1.1191	1.1195	1.1200	1.1204	1.1248	1.1295	1.1342	1.1914	1.2635	1.3388
450	1.1165	1.1167	1.1171	1,1175	1.1179	1.1220	1,1263	1.1307	1.1827	1.2464	1.3125
460	1.1142	1.1143	1.1147	1.1151	1.1155	1.1194	1.1233	1.1274	1.1749	1.2317	1.2902
470	1.1120	1.1122	1.1125	1.1129	1.1132	1.1168	1.1206	1.1244	1.1679	1.2189	1.2709
480	1.1100	1.1101	1.1104	1.1107	1.1111	1.1145	1.1179	1.1215	1.1616	1.2076	1.2543
490	1.1080	1.1081	1.1084	1.1087	1.1090	1.1122	1.1155	1.1188	1.1558	1.1976	1.2397
500	1.1061	1.1062	1.1065	1.1068	1.1071	1.1101	1.1131	1.1163	1.1506	1.1887	1.2269
510	1.1043	1.1044	1.1046	1.1049	1.1052	1.1000	1.1109	1.1139	1.1458	1.1807	1.2155
520	1.1026	1.1026	1.1029	1.1032	1.1034	1.1061	1.1088	1.1116	1.1413	1.1735	1.2053
530	1.1009	1.1010	1.1012	1.1015	1.1017	1.1043	1.1068	1.1094	1.1372	1.1669	1.1962
540	1.0993	1.0994	1.0997	1.0999	1.1001	1.1025	1.1049	1.1074	1.1334	1.1609	1.1879
550	1.0978	1.0979	1.0781	1.0984	1.0986	1.1008	1.1031	1.1055	1.1299	1.1555	1.1804
560	1.0964	1.0965	1.0967	1.0969	1.0971	1.0993	1.1014	1.1036	1.1266	1.1504	1.1736
570	1.0950	1.0951	1.0953	1.0955	1.0957	1.0977	1.0998	1.1019	1.1235	1.1458	1.1674
580	1.0937	1.0938	1.0939	1.0941	1.0943	1.0963	1.0982	1.1002	1.1206	1.1415	1.1616
590	1.0924	1.0925	1.0927	1.0928	1.0930	1.0949	1.0967	1.0986	1.1179	1.1375	1.1564
600	1.0912	1.0913	1.0914	1.0916	1.0918	1.0935	1.0953	1.0971	1.1154	1.1338	1.1515

TABLE 2.10

(Concluded)

P(Atm.) T(°K)	0.01	0.1	0.4	0.7	1	4	7	10	40	70	100
610	1.0900	1.0901	1.0902	1.0904	1.0906	1.0923	1.0940	1.0957	1.1130	1.1304	1.1470
620	1.0889	1.0890	1.0891	1.0893	1.0894	1.0910	1.0926	1.0943	1.1107	1.1272	1.1428
630	1.0878	1.0879	1.0880	1.0882	1.0883	1.0899	1.0914	1.0929	1.1086	1.1241	1.1389
640	1.0868	1.0868	1.0870	1.0871	1.0873	1.0887	1.0902	1.0917	1.1066	1.1213	1.1353
650	1.0858	1.0858	1.0860	1.0861	1.0862	1.0876	1.0890	1.0905	1.1047	1.1186	1.1319
660	1.0848	1.0848	1.0850	1.0851	1.0852	1.0866	1.0879	1.0893	1.1029	1.1161	1.1287
670	1.0839	1.0839	1.0840	1.0842	1.0843	1.0856	1.0869	1.0882	1.1011	1.1138	1.1257
680	1.0830	1.0830	1.0831	1.0833	1.0834	1.0846	1.0859	1.0871	1.0995	1.1115	1.1229
690	1.0821	1.0821	1.0823	1.0824	1.0825	1.0837	1.0849	1.0861	1.0979	1.1094	1.1203
700	1.0813	1.0813	1.0814	1.0815	1.0816	1.0828	1.0839	1.0851	1.0964	1.1074	1.1178
710	1.0805	1.0805	1.0806	1.0807	1.0808	1.0819	1.0830	1.0841	1.0950	1.1055	1.1154
720	1.0797	1.0797	1.0798	1.0799	1.0800	1.0811	1.0822	1.0832	1.0937	1.1037	1.1132
730	1.0789	1.0790	1.0791	1.0792	1.0793	1.0803	1.0813	1.0823	1.0924	1.1020	1.1111
740	1.0782	1.0782	1.0783	1.0784	1.0785	1.0795	1.0805	1.0815	1.0911	1.1004	1.1091
750	1.0775	1.0775	1.0776	1.0777	1.0778	1.0788	1.0797	1.0807	1.0900	1.0988	1.1071
760	1.0768	1.0768	1.0769	1.0770	1.0771	1.0780	1.0789	1.0799	1.0888	1.0973	1.1053
770	1.0762	1.0762	1.0763	1.0764	1.0764	1.0773	1.0782	1.0791	1.0877	1.0959	1.1036
780	1.0755	1.0755	1.0756	1.0757	1.0758	1.0767	1.0775	1.0784	1.0867	1.0946	1.1020
790	1.0749	1.0749	1.0750	1.0751	1.0752	1.0760	1.0768	1.0776	1.0857	1.0933	1.1004
800	1.0743	1.0743	1.0744	1.0745	1.0746	1.0754	1.0762	1.0770	1.0847	1.0920	1.0989
850	1.0716	1.0716	1.0717	1.0717	1.0718	1.0725	1.0732	1.0738	1.0804	1.0866	1.0924
900	1.0692	1.0693	1.0693	1.0694	1.0694	1.0700	1.0706	1.0712	1.0768	1.0821	1.0870
950	1.0672	1.0672	1.0673	1.0673	1.0674	1.0679	1.0684	1.0689	1.0738	1.0784	1.0827
1000	1.0655	1.0655	1.0655	1.0656	1.0556	1.0661	1.0665	1.0670	1.0712	1.0752	1.0790
1050	1.0639	1.0639	1.0640	1.0640	1.0641	1.0645	1.0649	1.0652	1.0690	1.0739	1.0759
1100	1.0626	1.0626	1.0626	1.0627	1.0627	1.0630	1.0634	1.0638	1.0671	1.0703	1.0732
1150	1.0614	1.0614	1.0614	1.0615	1.0615	1.0618	1.0621	1.0624	1.0655	1.0683	1.0710
1200	1.0603	1.0603	1.0604	1.0604	1.0604	1.0607	1.0610	1.0613	1.0640	1.0666	1.0690
1250	1.0594	1.0594	1.0594	1.0594	1.0595	1.0597	1.0600	1.0602	1.0627	1.0650	1.0672
1300	1.0585	1.0585	1.0586	1.0586	1.0586	1.0588	1.0591	1.0593	1.0616	1.0637	1.0657
1350	1.0578	1.0578	1.0578	1.0578	1.0578	1.0581	1.0583	1.0585	1.0606	1.0625	1.0644
1400	1.0571	1.0571	1.0571	1.0571	1.0572	1.0574	1.0576	1.0578	1.0597	1.0615	1.0632
1450	1.0565	1.0565	1.0565	1.0565	1.0565	1.0567	1.0569	1.0571	1.0589	1.0605	1.0621
1500	1.0559	1.0559	1.0559	1.0560	1.0560	1.0561	1.0563	1.0565	1.0581	1.0597	1.0611
273.16	1.1891	1.1898	1.1921	1.1944	1.1968	1.2231	1.2552	1.2954			
298.16	1.1736	1.1741	1.1757	1.1773	1.1790	1.1970	1.2178	1.2421	2.7437	2.8175	2.6447

TABLE 2.11

JOULE-THOMSON COEFFICIENT, μ, OF REAL GAS DIBORANE (REF. 2.16)

P(Atm.)	0.01	0.1	0.4	0.7	1	4	7	10	40	70	100
T(°K)											
130	14.6125										
140	11.9410										
150	9.8143										
160	8.1123	8.1043									
170	6.7436	6.7385	6.7253								
180	5.6383	5.6354	5.6285	5.6238							
190	4.7421	4.7410	4.7385	4.7373	4.7374						
200	4.0136	4.0131	4.0134	4.0145	4.0163						
210	3.4189	3.4187	3.4206	3.4230	3.4258	3.4864					
220	2.9307	2.9314	2.9342	2.9372	2.9405	2.9927					
230	2.5297	2.5304	2.5335	2.5368	2.5402	2.5860	2.6611				
240	2.1986	2.1990	2.2021	2.2053	2.2086	2.2489	2.3065	2.3911			
250	1.9233	1.9238	1.9267	1.9297	1.9328	1.9680	2.0138	2.0747			
260	1.6934	1.6941	1.6968	1.6995	1.7023	1.7328	1.7700	1.8161			
270	1.5007	1.5015	1.5039	1.5063	1.5087	1.5350	1.5656	1.6015			
280	1.3386	1.3391	1.3412	1.3432	1.3454	1.3679	1.3931	1.4216			
290	1.2008	1.2013	1.2031	1.2049	1.2067	1.2258	1.2467	1.2696			
300	1.0832	1.0837	1.0853	1.0868	1.0884	1.1046	1.1219	1.1404	1.3679	0.1790	0.0776
310	0.9826	0.9828	0.9841	0.9854	0.9868	1.0004	1.0148	1.0299	1.1934	0.3331	0.1053
320	0.8952	0.8957	0.8968	0.8979	0.8991	0.9105	0.9205	0.9346	1.0539	0.5498	0.1483
330	0.8196	0.8200	0.8210	0.8219	0.8229	0.8324	0.8422	0.8522	0.9404	0.6740	0.2116
340	0.7534	0.7539	0.7547	0.7555	0.7563	0.7643	0.7723	0.7804	0.8461	0.6942	0.2886
350	0.6958	0.6959	0.6965	0.6972	0.6978	0.7044	0.7110	0.7176	0.7664	0.6689	0.3568
360	0.6444	0.6446	0.6451	0.6457	0.6462	0.6516	0.6570	0.6622	0.6981	0.6288	0.3983
370	0.5986	0.5990	0.5994	0.5999	0.6003	0.6047	0.6091	0.6133	0.6391	0.5855	0.4139
380	0.5578	0.5583	0.5586	0.5590	0.5594	0.5629	0.5664	0.5697	0.5876	0.5435	0.4124
390	0.5218	0.5218	0.5221	0.5224	0.5226	0.5255	0.5282	0.5308	0.5424	0.5045	0.4012
400	0.4888	0.4889	0.4891	0.4893	0.4896	0.4918	0.4939	0.4958	0.5024	0.4687	0.3851
410	0.4594	0.4591	0.4592	0.4594	0.4596	0.4613	0.4629	0.4643	0.4668	0.4362	0.3668
420	0.4323	0.4320	0.4321	0.4322	0.4324	0.4336	0.4347	0.4357	0.4350	0.4067	0.3479
430	0.4079	0.4073	0.4073	0.4074	0.4075	0.4084	0.4092	0.4098	0.4065	0.3799	0.3292
440	0.3842	0.3846	0.3846	0.3847	0.3847	0.3853	0.3858	0.3861	0.3807	0.3557	0.3112
450	0.3636	0.3638	0.3638	0.3638	0.3638	0.3641	0.3643	0.3644	0.3573	0.3336	0.2941
460	0.3446	0.3445	0.3445	0.3446	0.3446	0.3446	0.3446	0.3444	0.3361	0.3135	0.2780
470	0.3266	0.3268	0.3268	0.3268	0.3267	0.3266	0.3264	0.3261	0.3167	0.2951	0.2629
480	0.3105	0.3103	0.3103	0.3103	0.3102	0.3099	0.3096	0.3091	0.2989	0.2782	0.2488
490	0.2953	0.2950	0.2950	0.2949	0.2949	0.2945	0.2939	0.2933	0.2825	0.2627	0.2357
500	0.2809	0.2808	0.2807	0.2806	0.2806	0.2800	0.2794	0.2787	0.2674	0.2484	0.2234
510	0.2678	0.2675	0.2674	0.2673	0.2672	0.2666	0.2659	0.2651	0.2535	0.2352	0.2120
520	0.2544	0.2550	0.2549	0.2548	0.2547	0.2540	0.2532	0.2524	0.2406	0.2230	0.2013
530	0.2429	0.2433	0.2432	0.2431	0.2430	0.2423	0.2414	0.2405	0.2286	0.2117	0.1914
540	0.2316	0.2323	0.2322	0.2321	0.2320	0.2312	0.2303	0.2294	0.2174	0.2012	0.1821
550	0.2219	0.2220	0.2219	0.2218	0.2217	0.2208	0.2199	0.2190	0.2070	0.1913	0.1734
560	0.2120	0.2123	0.2122	0.2121	0.2120	0.2111	0.2101	0.2091	0.1972	0.1822	0.1652
570	0.2028	0.2031	0.2030	0.2029	0.2028	0.2019	0.2009	0.1999	0.1881	0.1736	0.1575
580	0.1942	0.1944	0.1943	0.1942	0.1941	0.1932	0.1922	0.1912	0.1795	0.1655	0.1503
590	0.1858	0.1862	0.1861	0.1860	0.1859	0.1850	0.1840	0.1830	0.1714	0.1580	0.1435
600	0.1783	0.1785	0.1783	0.1783	0.1782	0.1772	0.1762	0.1752	0.1638	0.1509	0.1371

TABLE 2.11
(Concluded)

610	0.1707	0.1711	0.1710	0.1709	0.1708	0.1698	0.1688	0.1678	0.1567	0.1442	0.1311
620	0.1639	0.1641	0.1640	0.1639	0.1638	0.1628	0.1619	0.1609	0.1499	0.1379	0.1254
630	0.1573	0.1575	0.1574	0.1573	0.1572	0.1562	0.1552	0.1542	0.1435	0.1319	0.1200
640	0.1508	0.1512	0.1511	0.1510	0.1509	0.1499	0.1489	0.1480	0.1375	0.1262	0.1149
650	0.1452	0.1452	0.1450	0.1450	0.1449	0.1439	0.1430	0.1420	0.1317	0.1209	0.1100
660	0.1390	0.1394	0.1393	0.1392	0.1391	0.1382	0.1373	0.1363	0.1263	0.1158	0.1054
670	0.1336	0.1340	0.1338	0.1338	0.1337	0.1328	0.1318	0.1309	0.1211	0.1110	0.1011
680	0.1287	0.1288	0.1286	0.1286	0.1285	0.1276	0.1266	0.1257	0.1162	0.1065	0.0969
690	0.1234	0.1238	0.1237	0.1236	0.1235	0.1226	0.1217	0.1208	0.1115	0.1021	0.0930
700	0.1186	0.1190	0.1189	0.1188	0.1187	0.1179	0.1170	0.1161	0.1070	0.0980	0.0892
710	0.1143	0.1145	0.1144	0.1143	0.1142	0.1133	0.1125	0.1116	0.1028	0.0940	0.0856
720	0.1101	0.1101	0.1100	0.1099	0.1099	0.1090	0.1082	0.1073	0.0987	0.0902	0.0821
730	0.1058	0.1060	0.1058	0.1058	0.1057	0.1048	0.1040	0.1032	0.0948	0.0866	0.0789
740	0.1018	0.1020	0.1018	0.1018	0.1017	0.1009	0.1001	0.0992	0.0911	0.0832	0.0757
750	0.0976	0.0981	0.0980	0.0979	0.0978	0.0971	0.0963	0.0955	0.0876	0.0799	0.0727
760	0.0943	0.0945	0.0943	0.0942	0.0942	0.0934	0.0926	0.0918	0.0841	0.0768	0.0698
770	0.0906	0.0909	0.0908	0.0907	0.0906	0.0899	0.0891	0.0884	0.0809	0.0737	0.0671
780	0.0871	0.0875	0.0874	0.0873	0.0872	0.0865	0.0858	0.0850	0.0778	0.0708	0.0644
790	0.0842	0.0842	0.0841	0.0840	0.0840	0.0833	0.0825	0.0818	0.0747	0.0681	0.0619
800	0.0811	0.0811	0.0810	0.0809	0.0808	0.0801	0.0794	0.0787	0.0719	0.0654	0.0594
850	0.0667	0.0670	0.0669	0.0668	0.0668	0.0662	0.0655	0.0649	0.0590	0.0535	0.0485
900	0.0552	0.0552	0.0551	0.0551	0.0550	0.0545	0.0539	0.0534	0.0483	0.0436	0.0394
950	0.0458	0.0453	0.0452	0.0451	0.0451	0.0446	0.0441	0.0436	0.0392	0.0353	0.0317
1000	0.0370	0.0367	0.0366	0.0366	0.0365	0.0361	0.0357	0.0353	0.0315	0.0281	0.0251
1050	0.0289	0.0293	0.0292	0.0292	0.0291	0.0288	0.0284	0.0281	0.0248	0.0209	0.0194
1100	0.0231	0.0229	0.0228	0.0227	0.0227	0.0224	0.0221	0.0218	0.0190	0.0165	0.0144
1150	0.0167	0.0171	0.0171	0.0171	0.0171	0.0168	0.0165	0.0163	0.0139	0.0118	0.0100
1200	0.0119	0.0121	0.0121	0.0121	0.0120	0.0118	0.0116	0.0114	0.0093	0.0076	0.0060
1250	0.0072	0.0076	0.0076	0.0076	0.0076	0.0074	0.0072	0.0070	0.0053	0.0038	0.0025
1300	0.0040	0.0036	0.0036	0.0036	0.0036	0.0034	0.0032	0.0031	0.0016	0.0004	- 0.0007
1350	0.0000	0.0000	0.0000	0.0000	- 0.0001	- 0.0002	- 0.0003	- 0.0005	- 0.0017	- 0.0027	- 0.0035
1400	- 0.0034	- 0.0033	- 0.0033	- 0.0033	- 0.0033	- 0.0034	- 0.0036	- 0.0037	- 0.0047	- 0.0055	- 0.0062
1450	- 0.0063	- 0.0063	- 0.0063	- 0.0063	- 0.0063	- 0.0064	- 0.0065	- 0.0066	- 0.0074	- 0.0081	- 0.0086
1500	- 0.0092	- 0.0090	- 0.0091	- 0.0091	- 0.0091	- 0.0091	- 0.0092	- 0.0093	- 0.0099	- 0.0104	- 0.0108
273.16	1.4464	1.4472	1.4495	1.4518	1.4541	1.4792	1.5079	1.5412			
298.16	1.1037	1.1040	1.1056	1.1072	1.1088	1.1255	1.1434	1.1627	1.4034	0.1601	0.0735

TABLE 2.12

THERMAL FUNCTIONS FOR SATURATED DIBORANE (REF. 2.16)

T(°K)	Pressure (atm)	Enthalpy $H-E^\circ_0/RT$		Entropy S/R	
		Vapor	Liquid	Vapor	Liquid
130	0.01672	4.0456	-11.213	27.661	12.403
132	.02106	4.0474	-10.897	27.495	12.550
134	.02633	4.0491	-10.593	27.336	12.693
136	.03266	4.0507	-10.299	27.183	12.833
138	.04023	4.0522	-10.015	27.037	12.970
140	0.04920	4.0535	- 9.7395	26.897	13.104
142	.05979	4.0546	- 9.4727	26.763	13.235
144	.07220	4.0556	- 9.2140	26.634	13.364
146	.08668	4.0563	- 8.9630	26.510	13.491
148	.10347	4.0568	- 8.7193	26.391	13.615
150	0.12284	4.0571	- 8.4825	26.277	13.738
152	.14508	4.0572	- 8.2521	26.168	13.859
154	.17051	4.0570	- 8.0280	26.062	13.977
156	.19945	4.0565	- 7.8097	25.962	14.095
158	.23225	4.0557	- 7.5970	25.864	14.212
160	0.26928	4.0547	- 7.3897	25.771	14.327
162	.31091	4.0533	- 7.1874	25.681	14.440
164	.35755	4.0517	- 6.9898	25.594	14.553
166	.40962	4.0497	- 6.7969	25.511	14.665
168	.46756	4.0474	- 6.6084	25.431	14.775
170	0.53182	4.0448	- 6.4240	25.354	14.885
172	.60287	4.0418	- 6.2437	25.279	14.994
174	.68119	4.0385	- 6.0671	25.208	15.102
176	.76729	4.0349	- 5.8942	25.139	15.210
178	.86168	4.0309	- 5.7248	25.072	15.316
180	0.96489	4.0266	- 5.5587	25.008	15.423
182	1.0775	4.0219	- 5.3958	24.946	15.529
184	1.1999	4.0169	- 5.2360	24.887	15.634
186	1.3329	4.0115	- 5.0792	24.830	15.739
188	1.4769	4.0058	- 4.9251	24.774	15.844
190	1.6325	3.9997	- 4.7738	24.721	15.948
192	1.8004	3.9932	- 4.6252	24.670	16.052
194	1.9811	3.9864	- 4.4790	24.621	16.155
196	2.1752	3.9793	- 4.3352	24.573	16.259
198	2.3834	3.9717	- 4.1937	24.527	16.362
200	2.6063	3.9638	- 4.0545	24.483	16.465
202	2.8445	3.9555	- 3.9175	24.441	16.568
204	3.0987	3.9469	- 3.7825	24.400	16.670
206	3.3694	3.9378	- 3.6495	24.360	16.773
208	3.6574	3.9284	- 3.5184	24.322	16.876
210	3.9634	3.9186	- 3.3891	24.286	16.978
212	4.2878	3.9084	- 3.2617	24.251	17.081
214	4.6315	3.8977	- 3.1359	24.217	17.183
216	4.9951	3.8866	- 3.0118	24.184	17.286
218	5.3792	3.8751	- 2.8893	24.153	17.389

TABLE 2.12
(Concluded)

T(°K)	Pressure (atm)	Enthalpy $H-E_0^\circ/RT$		Entropy S/R	
		Vapor	Liquid	Vapor	Liquid
220	5.7846	3.8632	-2.7683	24.123	17.492
222	6.2119	3.8507	-2.6488	24.094	17.595
224	6.6619	3.8378	-2.5306	24.066	17.698
226	7.1351	3.8244	-2.4138	24.040	17.801
228	7.6323	3.8104	-2.2983	24.014	17.905
230	8.1543	3.7959	-2.1840	23.989	18.009
232	8.7017	3.7808	-2.0708	23.966	18.114
234	9.2752	3.7650	-1.9588	23.943	18.219
236	9.8757	3.7486	-1.8477	23.921	18.325
238	10.504	3.7315	-1.7377	23.900	18.431
240	11.160	3.7137	-1.6285	23.880	18.537
242	11.846	3.6951	-1.5201	23.860	18.645
244	12.562	3.6756	-1.4124	23.841	18.753
246	13.308	3.6552	-1.3054	23.823	18.863
248	14.087	3.6338	-1.1989	23.806	18.973
250	14.897	3.6112	-1.0928	23.789	19.085
252	15.741	3.5876	-0.98706	23.772	19.198
254	16.620	3.5626	-0.88151	23.756	19.312
256	17.533	3.5361	-0.77600	23.741	19.429
258	18.483	3.5081	-0.67037	23.726	19.547
260	19.470	3.4783	-0.56441	23.711	19.668
262	20.496	3.4466	-0.45792	23.696	19.791
264	21.561	3.4126	-0.35061	23.681	19.918
266	22.667	3.3761	-0.24218	23.667	20.048
268	23.814	3.3366	-0.13225	23.652	20.183
270	25.005	3.2938	-0.02035	23.637	20.323
272	26.241	3.2470	0.09409	23.622	20.469
274	27.522	3.1955	0.21183	23.606	20.623
276	28.851	3.1381	0.33384	23.590	20.785
278	30.230	3.0735	0.46149	23.572	20.960
280	31.659	2.9994	0.59668	23.552	21.149
282	33.141	2.9124	0.74241	23.530	21.360
284	34.679	2.8067	0.90369	23.505	21.602
286	36.273	2.6699	1.0905	23.473	21.893
288	37.927	2.4675	1.3294	23.428	22.290
289.86	39.520	1.8408	1.8408	23.307	23.307

TA

IDEAL HEAT CAPACITY AND LOW-PRESS

(M = 27.69, σ = 4.821,

Temperature, K	Heat Capacity, C_p/R	Viscosity x 10^6, poises	Translational Thermal Conductivity x 10^6, g-cal/cm-sec-K	Internal Thermal Conductivity x 10^6, g-cal/cm-sec-K	Total Thermal Conductivity x 10^6, g-cal/cm-sec-K
100	4.144	26.0	7.0	4.0	11.0
200	5.025	52.1	14.0	12.5	26.5
300	6.731	77.6	20.9	31.1	52.0
400	8.659	100.7	27.1	58.7	85.8
500	10.439	121.5	32.7	91.3	124.0
600	12.003	140.5	37.8	126.5	164.3
700	13.354	158.1	42.5	162.5	205.1
800	14.509	174.5	47.0	198.6	245.5
900	15.490	190.1	51.2	233.9	285.1
1000	16.319	204.8	55.1	268.1	323.2
1100	17.020	218.8	58.9	301.0	359.9
1200	17.612	232.3	62.5	332.6	395.1
1300	18.115	245.4	66.0	362.9	429.0
1400	18.542	258.0	69.4	392.1	461.5
1500	18.908	270.3	72.7	420.1	492.9
1600	19.222	282.2	76.0	447.1	523.0
1700	19.493	293.9	79.1	473.0	552.1
1800	19.728	305.2	82.1	498.1	580.2
1900	19.933	316.2	85.1	522.2	607.3
2000	20.112	327.0	88.0	545.6	633.6
2100	20.270	337.5	90.8	568.2	659.1
2200	20.410	347.8	93.6	590.2	683.8
2300	20.534	358.0	96.3	611.5	707.9
2400	20.644	367.9	99.0	632.3	731.3
2500	20.742	377.6	101.6	652.6	754.2
2600	20.831	387.2	104.2	672.5	776.7
2700	20.910	396.7	106.8	691.9	798.7
2800	20.982	406.1	109.3	711.0	8203
2900	21.048	415.4	111.8	729.9	841.7
3000	21.107	424.6	114.3	748.5	862.7
3100	21.161	433.8	116.7	766.9	883.6
3200	21.210	442.9	119.2	7851	904.3
3300	21.255	452.1	121.7	803.2	924.9
3400	21.297	461.2	124.1	821.3	945.4
3500	21.335	470.1	126.5	838.8	965.3
3600	21.370	478.8	128.9	856.0	984.8
3700	21.402	487.5	131.2	872.9	1004.1
3800	21.432	496.1	133.5	889.7	1023.2
3900	21.460	504.5	135.8	906.2	1042.0
4000	21.486	512.9	138.0	922.6	1060.6
4100	21.510	521.3	140.3	938.7	1079.0
4200	21.532	529.5	142.5	954.7	1097.2
4300	21.553	537.7	144.7	970.5	1115.2
4400	21.573	545.8	146.9	986.2	1133.0
4500	21.591	553.8	149.0	1001.6	1150.7
4600	21.608	561.8	151.2	1016.9	1168.1
4700	21.625	569.7	153.3	1032.1	1185.4
4800	21.640	577.5	155.4	1047.2	1202.6
4900	21.654	585.3	157.5	1062.0	1219.6
5000	21.667	593.0	159.6	1076.8	1236.4

FOLDOUT FRAME 1

BLE 2.13

URE TRANSPORT PROPERTIES OF DIBORANE

ε/k = 213.2) (Ref. 2.31)

Temperature, R	Heat Capacity, C_p/R	Viscosity x 10^6, lbm/ft-sec	Translational Thermal Conductivity x 10^3, Btu/ft-hr-F	Internal Thermal Conductivity x 10^3, Btu/ft-hr-F	Total Thermal Conductivity x 10^3, Btu/ft-hr-F
180	4.144	1.7	1.7	0.97	2.7
360	5.025	3.5	3.4	3.0	6.4
540	6.731	5.2	5.1	7.5	12.6
720	8.659	6.8	6.6	14.1	20.8
900	10.439	8.2	7.9	22.1	30.0
1080	12.003	9.4	9.1	30.6	39.7
1260	13.354	10.6	10.3	39.3	49.6
1440	14.509	11.7	11.4	48.0	59.4
1620	15.490	12.8	12.4	56.6	69.0
1800	16.319	13.8	13.3	64.8	78.2
1980	17.020	14.7	14.2	72.8	87.0
2160	17.612	15.6	15.1	80.4	95.6
2340	18.115	16.5	16.0	87.8	103.8
2520	18.542	17.3	16.8	94.8	111.6
2700	18.908	18.2	17.6	101.6	119.2
2880	19.222	19.0	18.4	108.1	126.5
3060	19.493	19.8	19.1	114.4	133.5
3240	19.728	20.5	19.9	120.5	140.3
3420	19.933	21.2	20.6	126.3	146.9
3600	20.112	22.0	21.3	132.0	153.2
3780	20.270	22.7	22.0	137.4	159.4
3960	20.410	23.4	22.6	142.7	165.4
4140	20.534	24.1	23.3	147.9	171.2
4320	20.644	24.7	23.9	152.9	176.9
4500	20.742	25.4	24.6	157.8	182.4
4680	20.831	26.0	25.2	162.7	187.9
4860	20.910	26.7	25.8	167.3	193.2
5040	20.982	27.3	26.4	172.0	198.4
5220	21.048	27.9	27.0	176.5	203.6
5400	21.107	28.5	27.6	181.0	208.7
5580	21.161	29.2	28.2	185.5	213.7
5760	21.210	29.8	28.8	189.9	218.7
5940	21.255	30.4	29.4	194.3	223.7
6120	21.297	31.0	30.0	198.6	228.7
6300	21.335	31.6	30.6	202.9	233.5
6480	21.370	32.2	31.2	207.0	238.2
6660	21.402	32.8	31.7	211.1	242.1
6840	21.432	33.3	32.3	215.2	247.5
7020	21.460	33.9	32.8	219.2	252.0
7200	21.486	34.5	33.4	223.1	256.5
7380	21.510	35.0	33.9	227.0	261.0
7560	21.532	35.6	34.5	230.9	265.4
7740	21.553	36.1	35.0	234.7	269.7
7920	21.573	36.7	35.5	238.5	274.0
8100	21.591	37.2	36.0	242.2	278.3
8280	21.608	37.8	36.6	245.9	282.5
8460	21.625	38.3	37.1	249.6	286.7
8640	21.640	38.8	37.6	253.3	290.0
8820	21.654	39.3	38.1	256.9	295.0
9000	21.667	39.8	38.6	260.4	299.0

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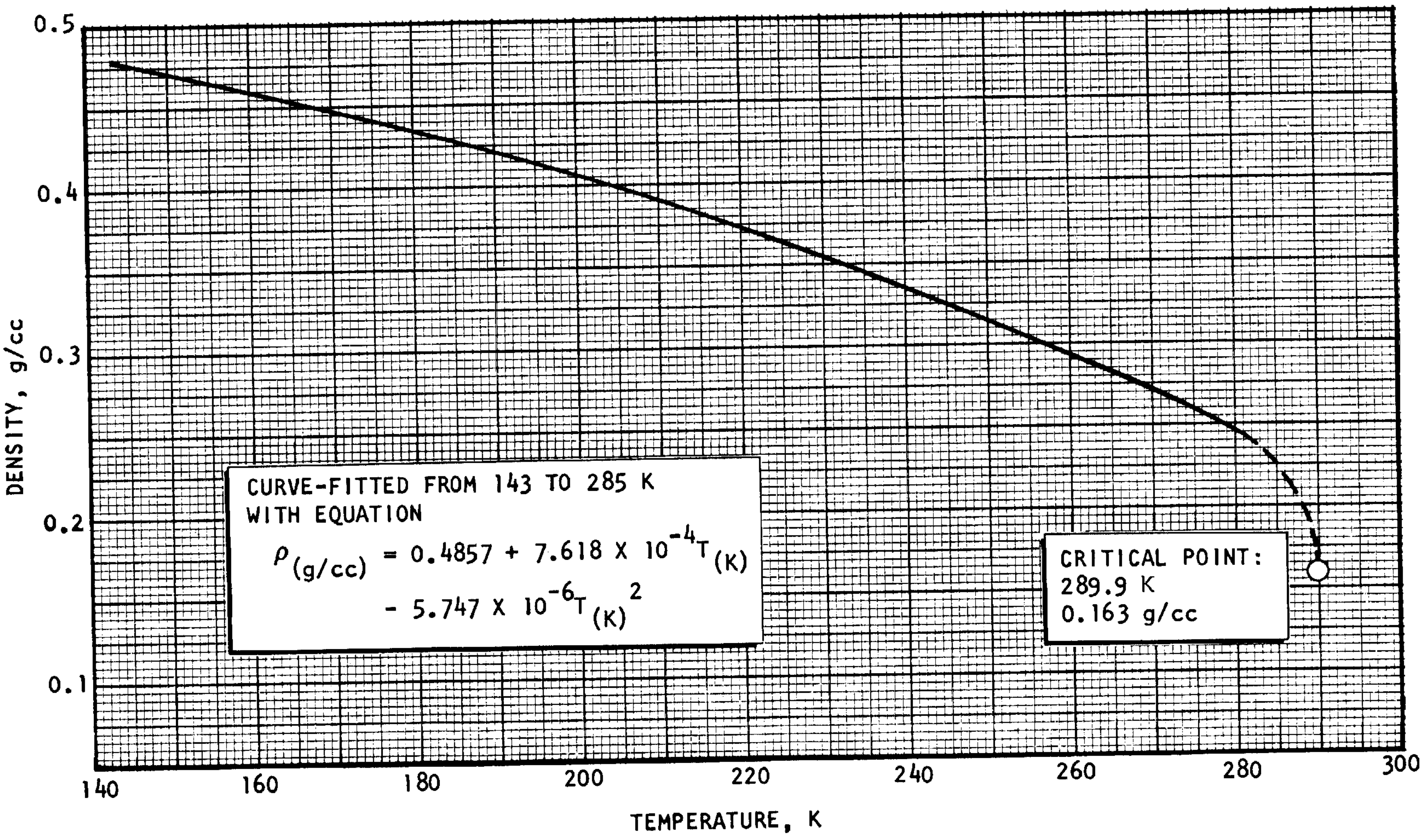


Figure 2.1. Density of Saturated Liquid Diborane (Correlated from Data of Ref. 2.11-2.13)

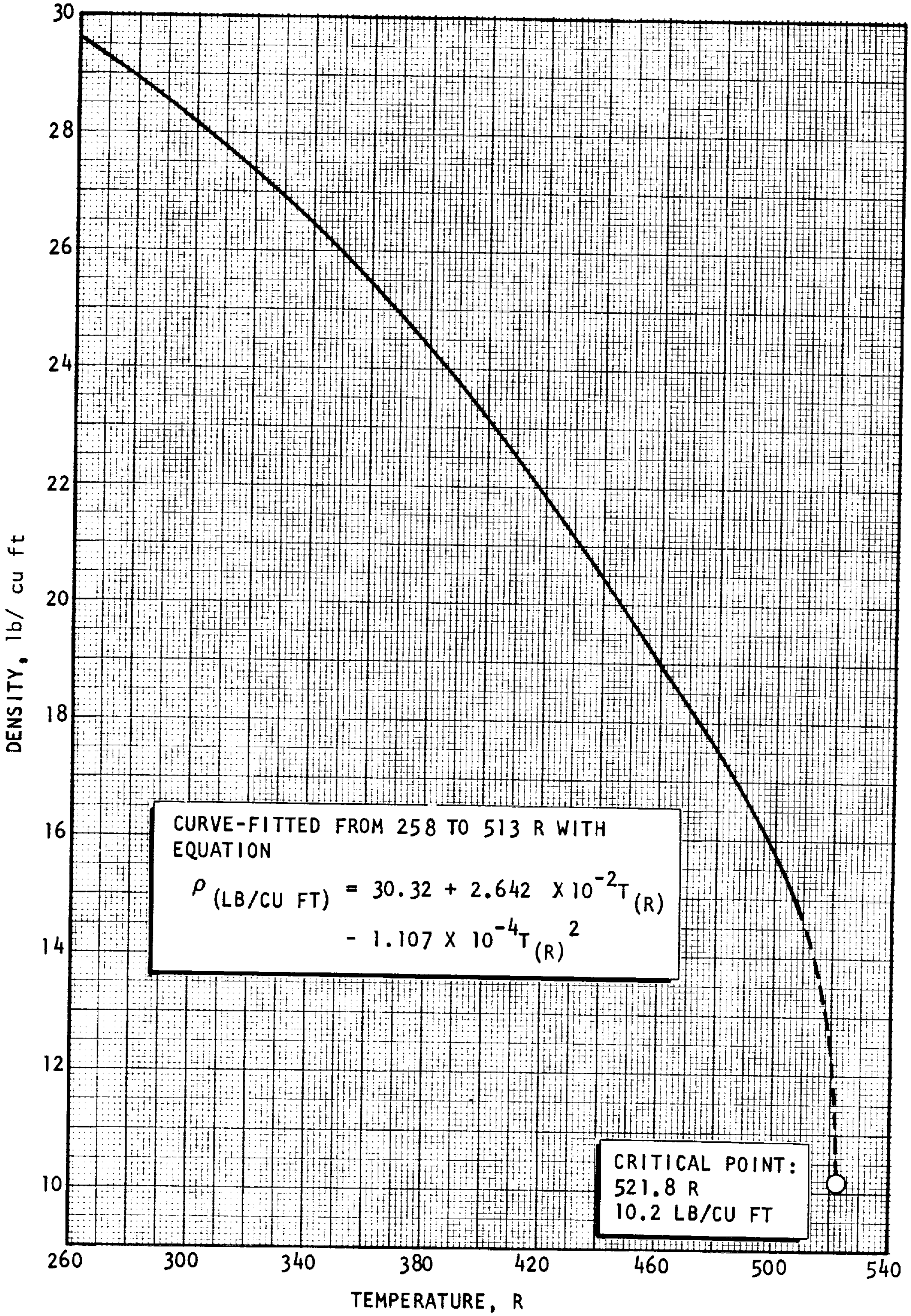


Figure 2.1a. Density of Saturated Liquid Diborane (Correlated from Data of Ref. 2.11-2.13)

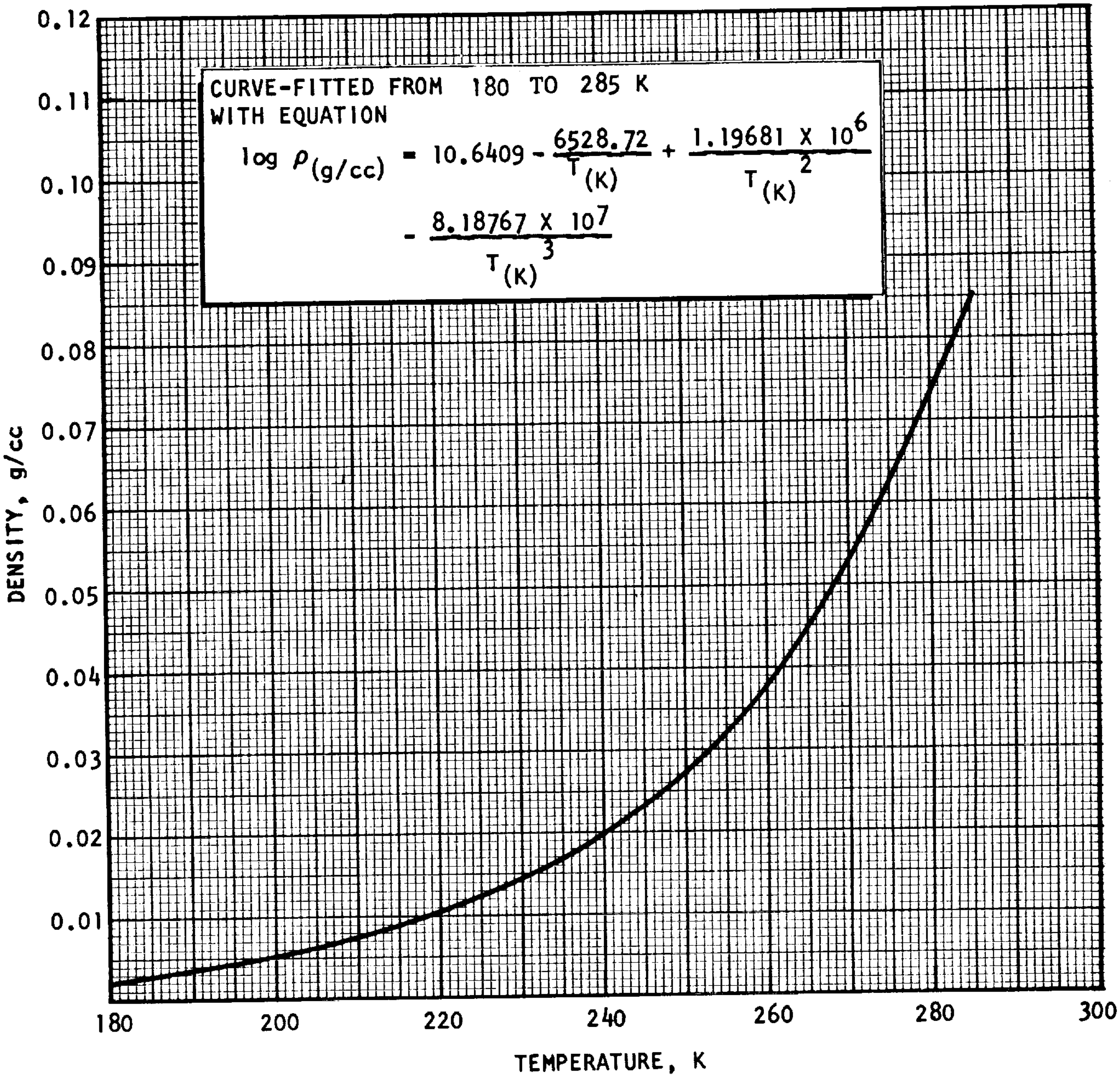
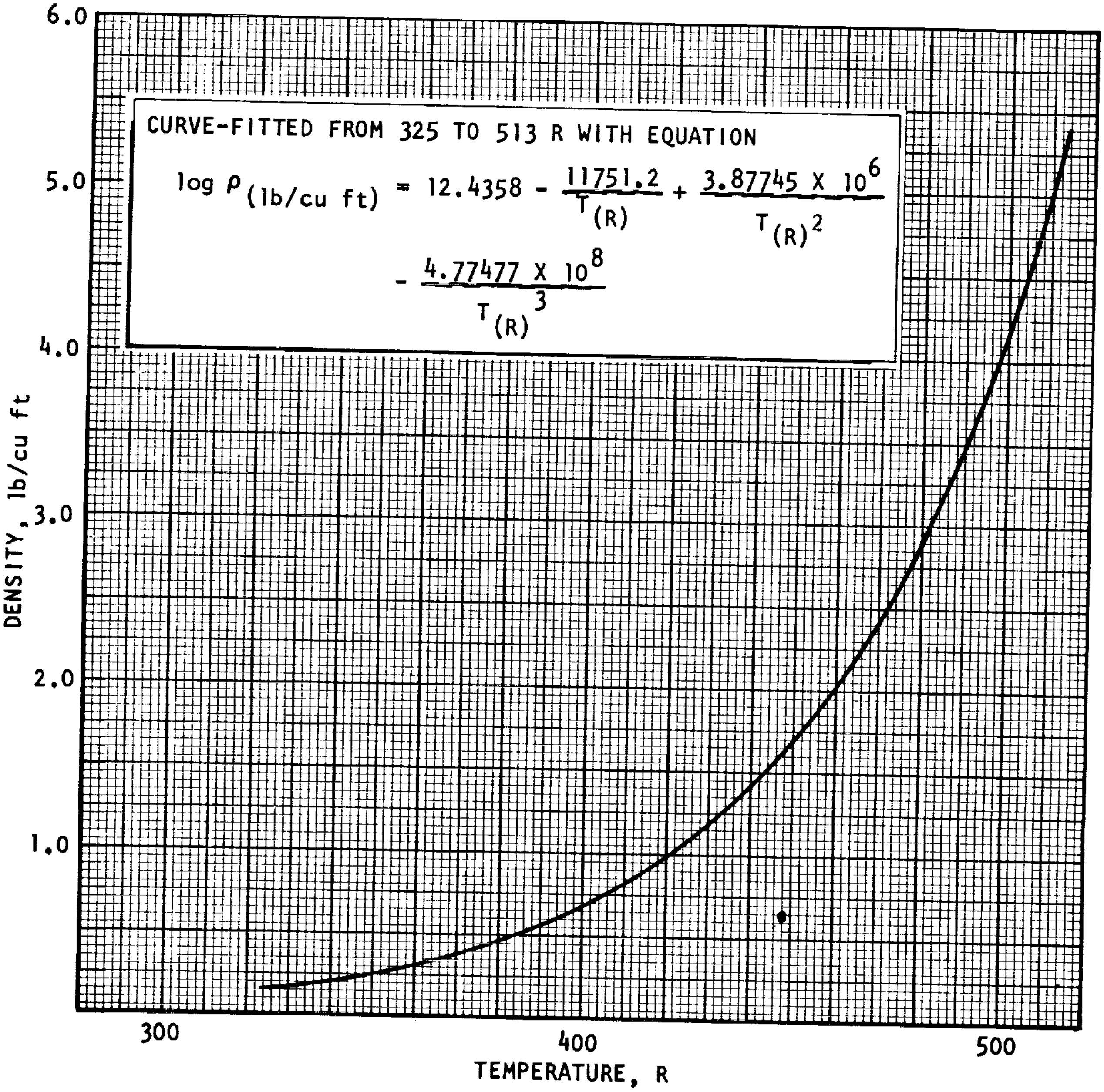


Figure 2.1b. Saturated Vapor Density of Diborane (Correlated from Data of Ref. 2.14a)



CURVE-FITTED FROM 325 TO 513 R WITH EQUATION

$$\log \rho_{(\mathrm{lb/cu\ ft})} = 12.4358 - \frac{11751.2}{T_{(R)}} + \frac{3.87745 \times 10^{6}}{T_{(R)}^{2}} - \frac{4.77477 \times 10^{8}}{T_{(R)}^{3}}$$

Figure 2.1c. Saturated Vapor Density of Diborane (Correlated from Data of Ref. 2.14a)

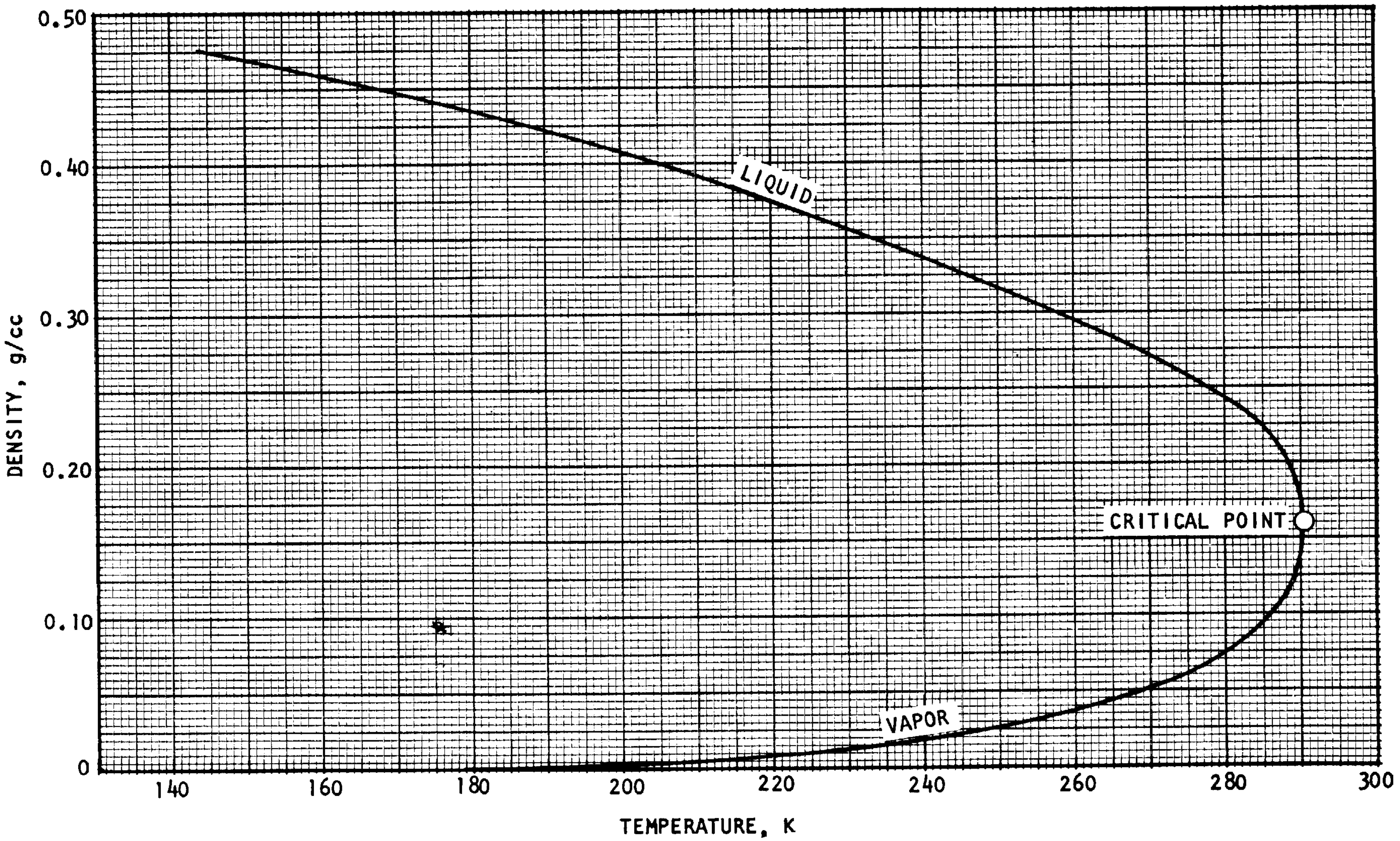


Figure 2.1d. Density of Saturated Liquid and Vapor Diborane (Data Composite from Fig. 2.1 and 2.1b)

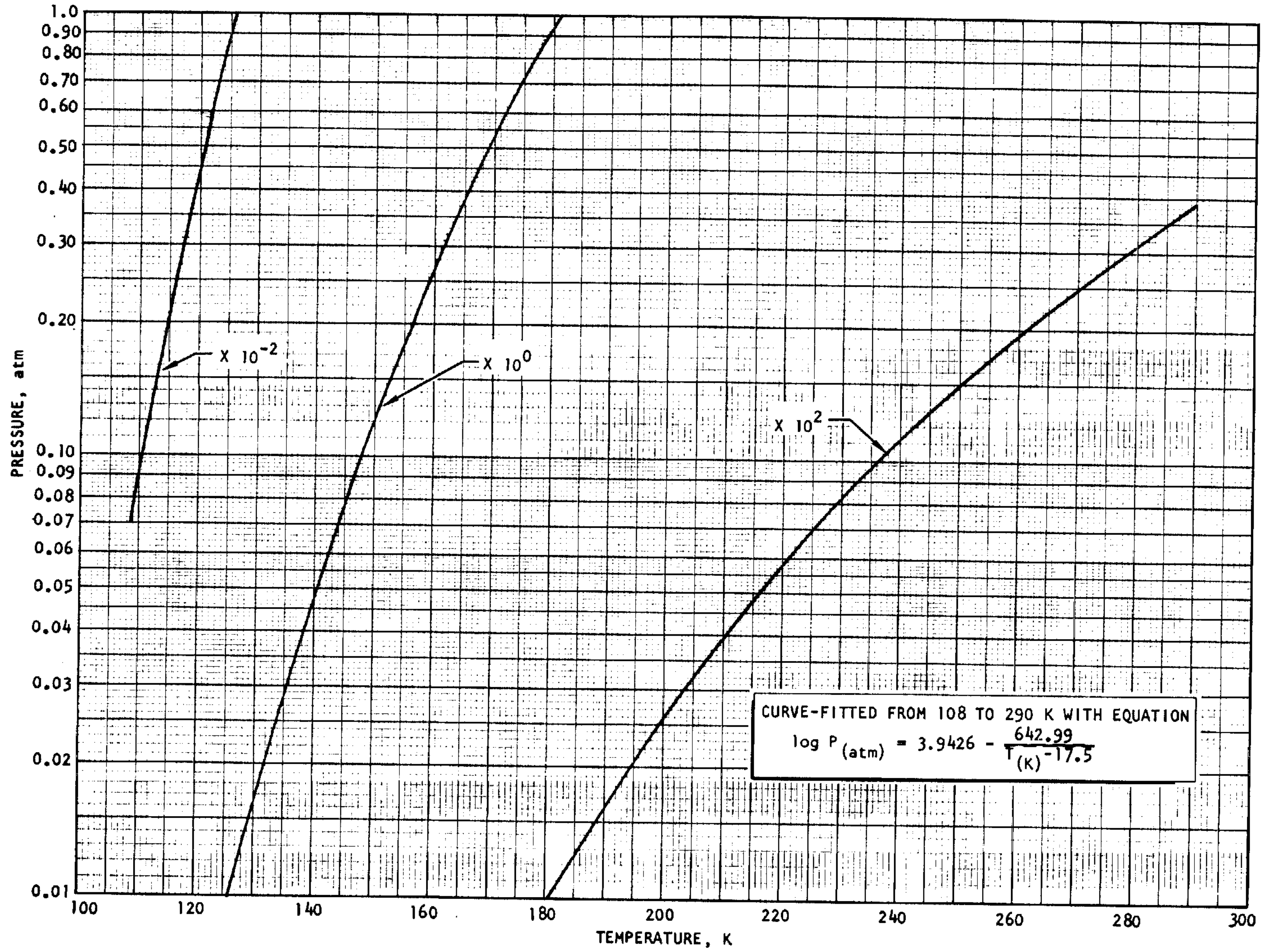
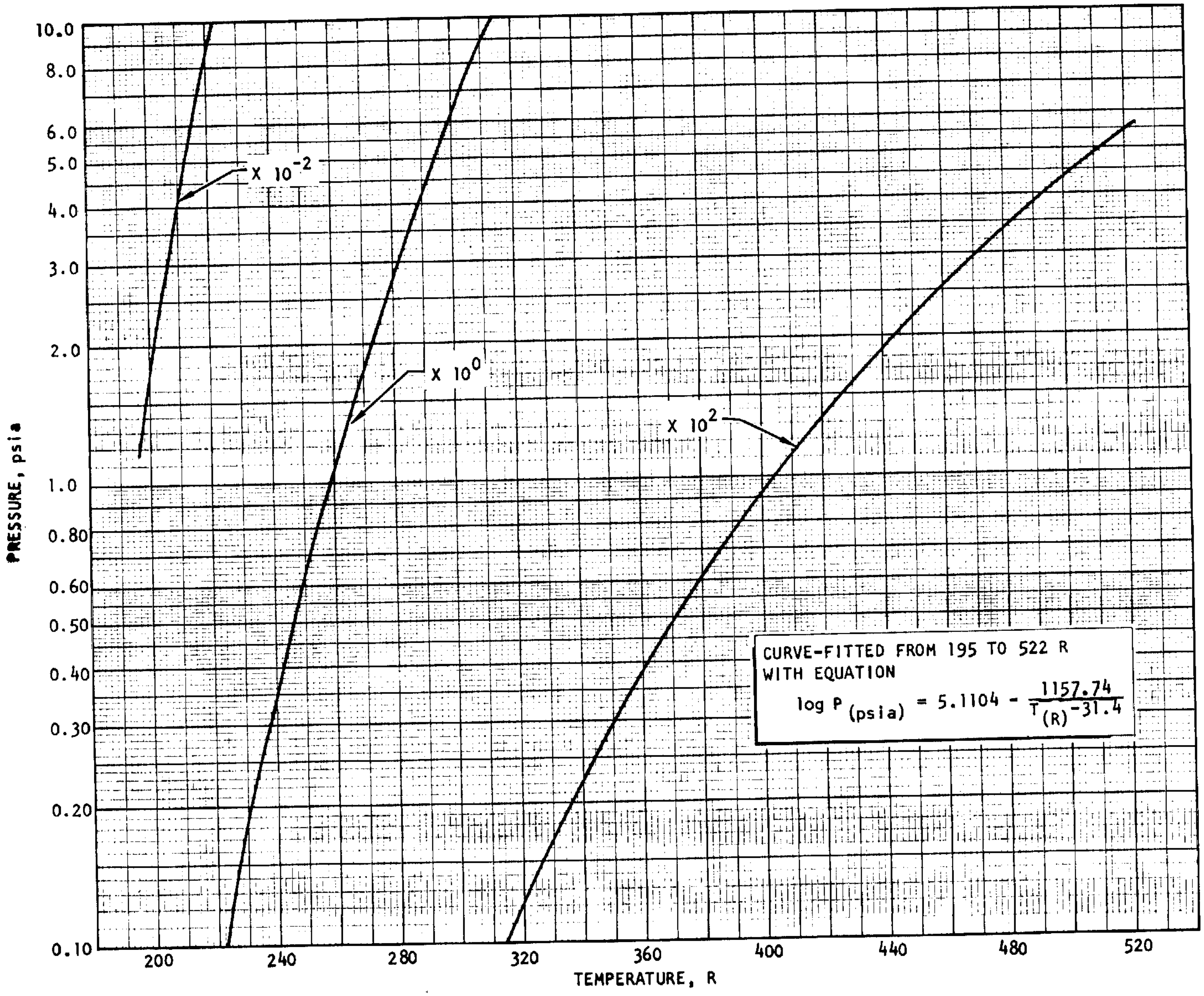


Figure 2.2. Vapor Pressure of Diborane (Correlated from data of Ref. 2.3, 2.4, 2.6-2.8)



CURVE-FITTED FROM 195 TO 522 R
WITH EQUATION

$$\log P_{(\mathrm{psia})} = 5.1104 - \frac{1157.74}{T_{(R)} - 31.4}$$

Figure 2.2a. Vapor Pressure of Diborane (Correlated from data of Ref. 2.3, 2.4, 2.6-2.8)

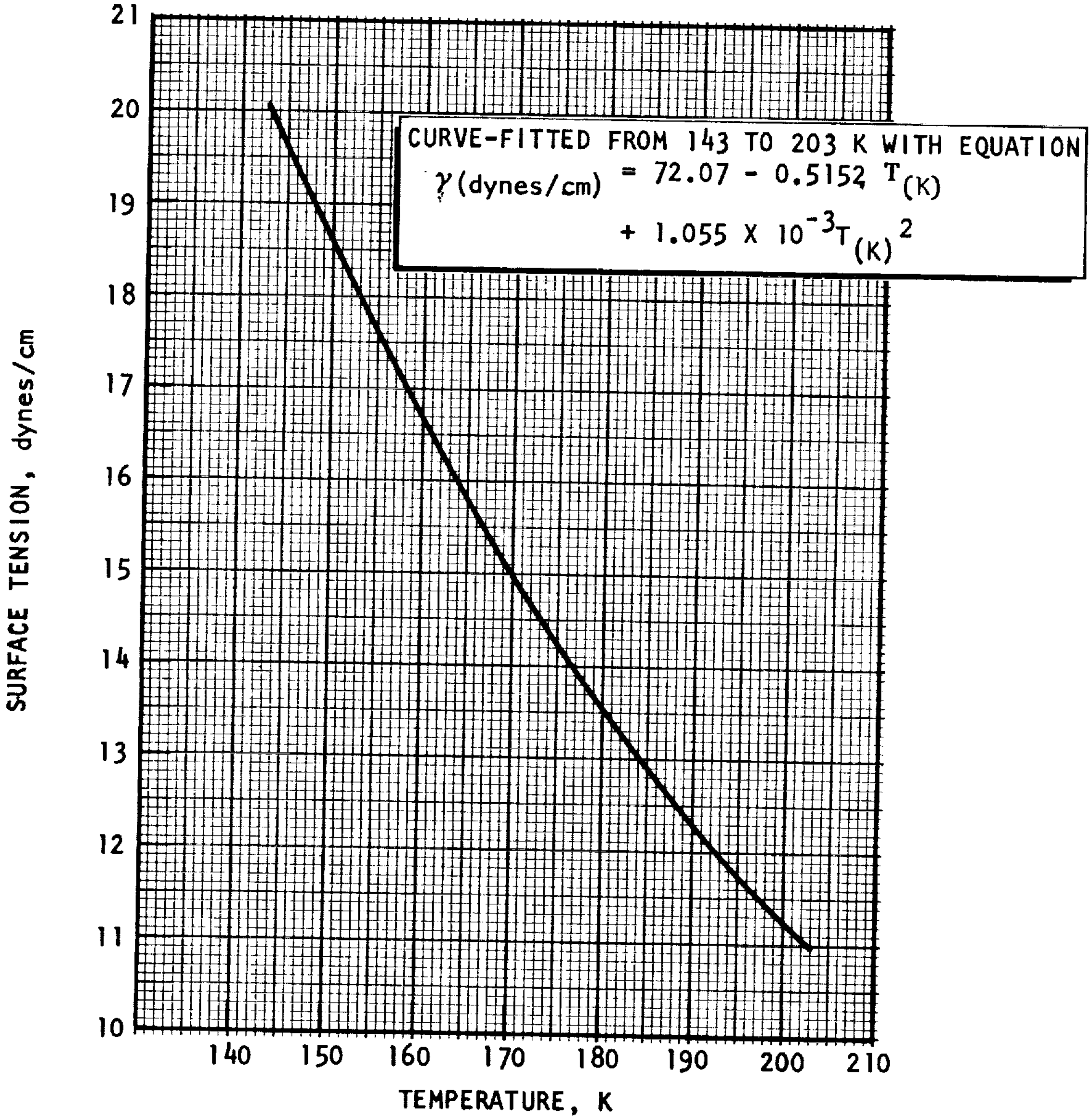


Figure 2.3. Surface Tension of Saturated Liquid Diborane (Correlated from Data of Ref. 2.11-2.13)

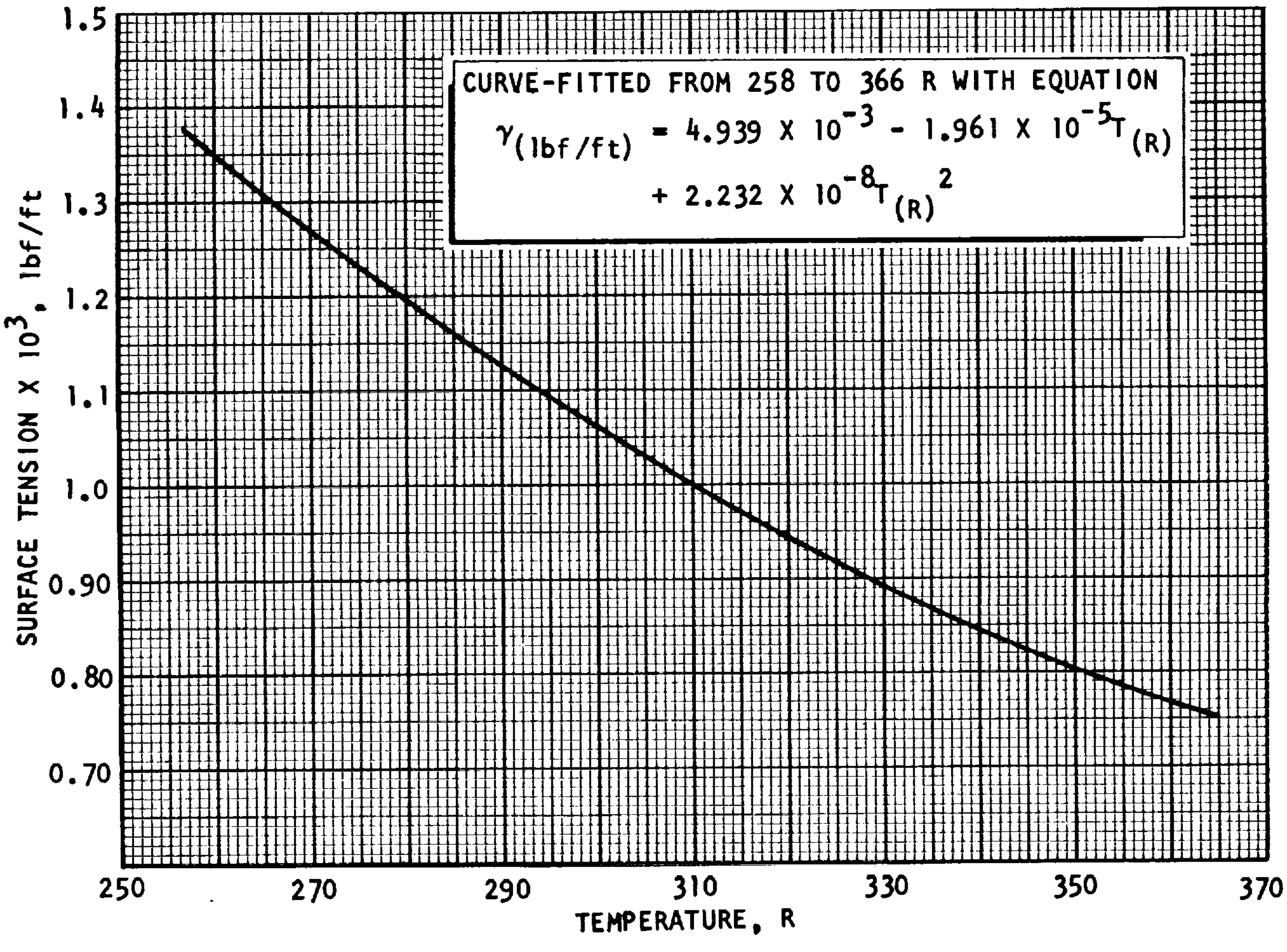


Figure 2.3a. Surface Tension of Saturated Liquid Diborane (Correlated from Data of Ref. 2.11-2.13)

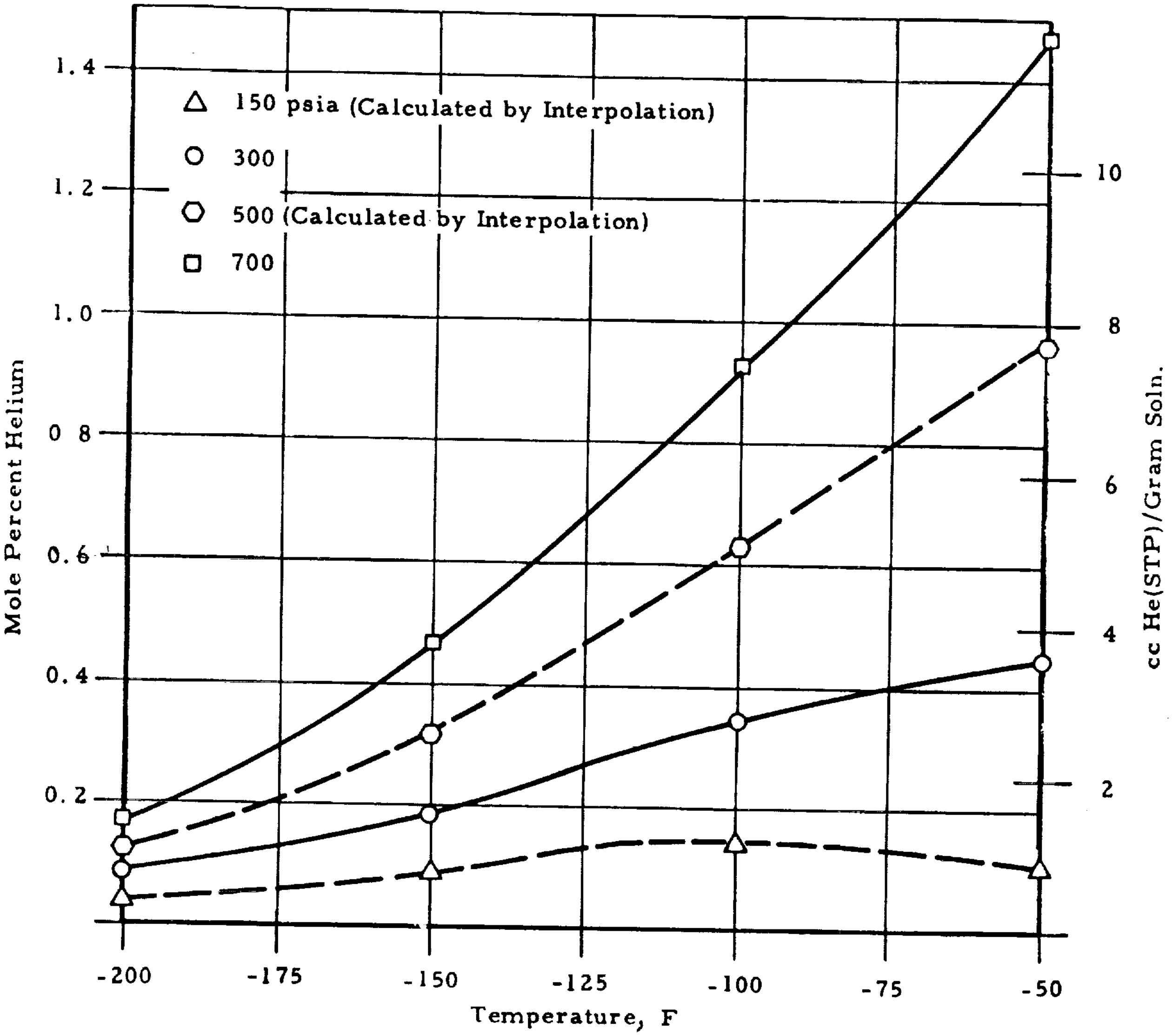


Figure 2.4. Isobaric Temperature-Composition Diagram for the System Liquid Diborane-Helium (Reprinted from Ref. 2.19)

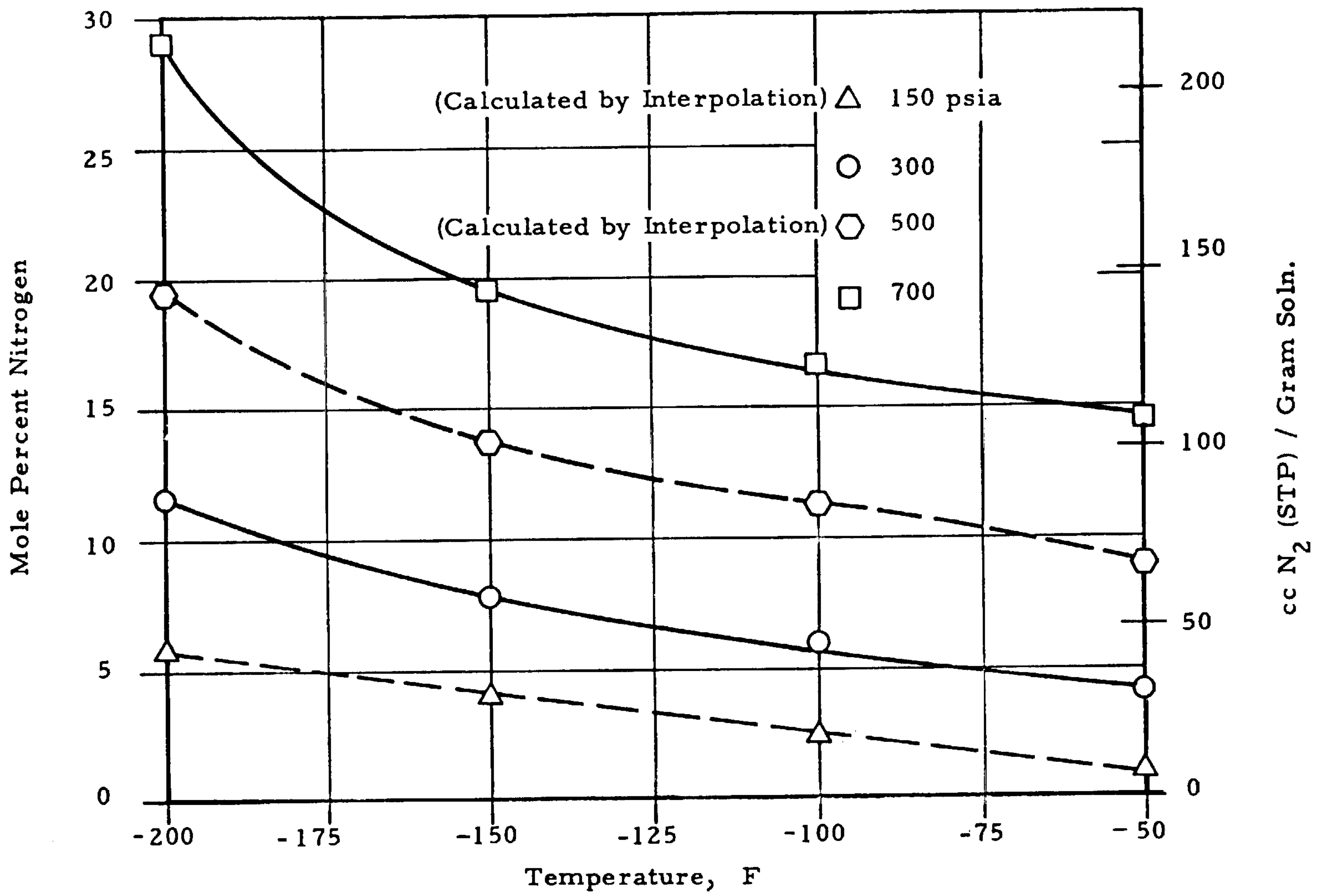


Figure 2.4a. Isobaric Temperature-Composition Diagram For the System Liquid Diborane-Nitrogen (Reprinted from Ref. 2.19)

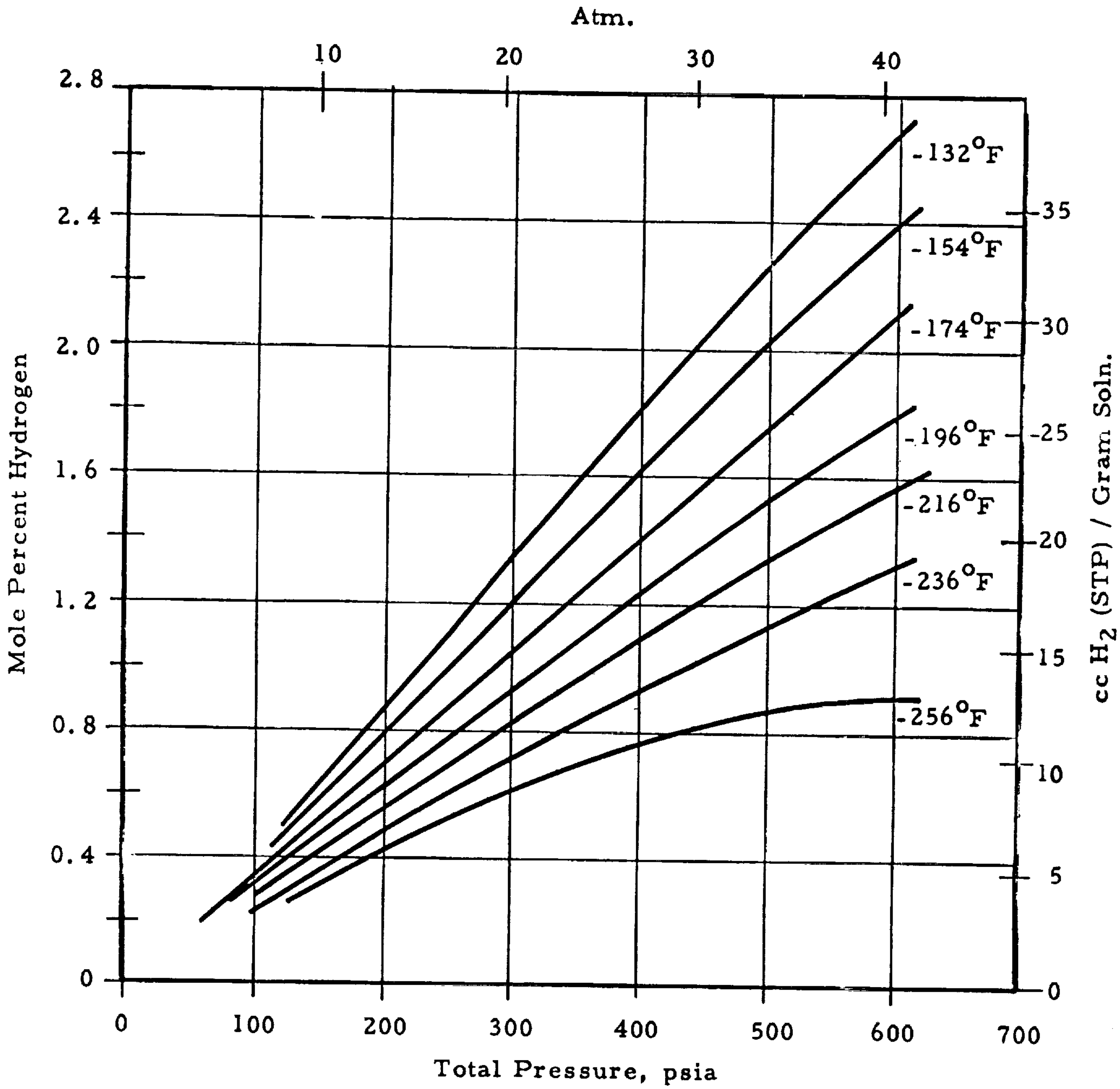


Figure 2.4b. Isothermal Pressure-Composition Diagram for the System Liquid Diborane-Hydrogen (Reprinted from Ref. 2.10 from data of Ref. 2.20)

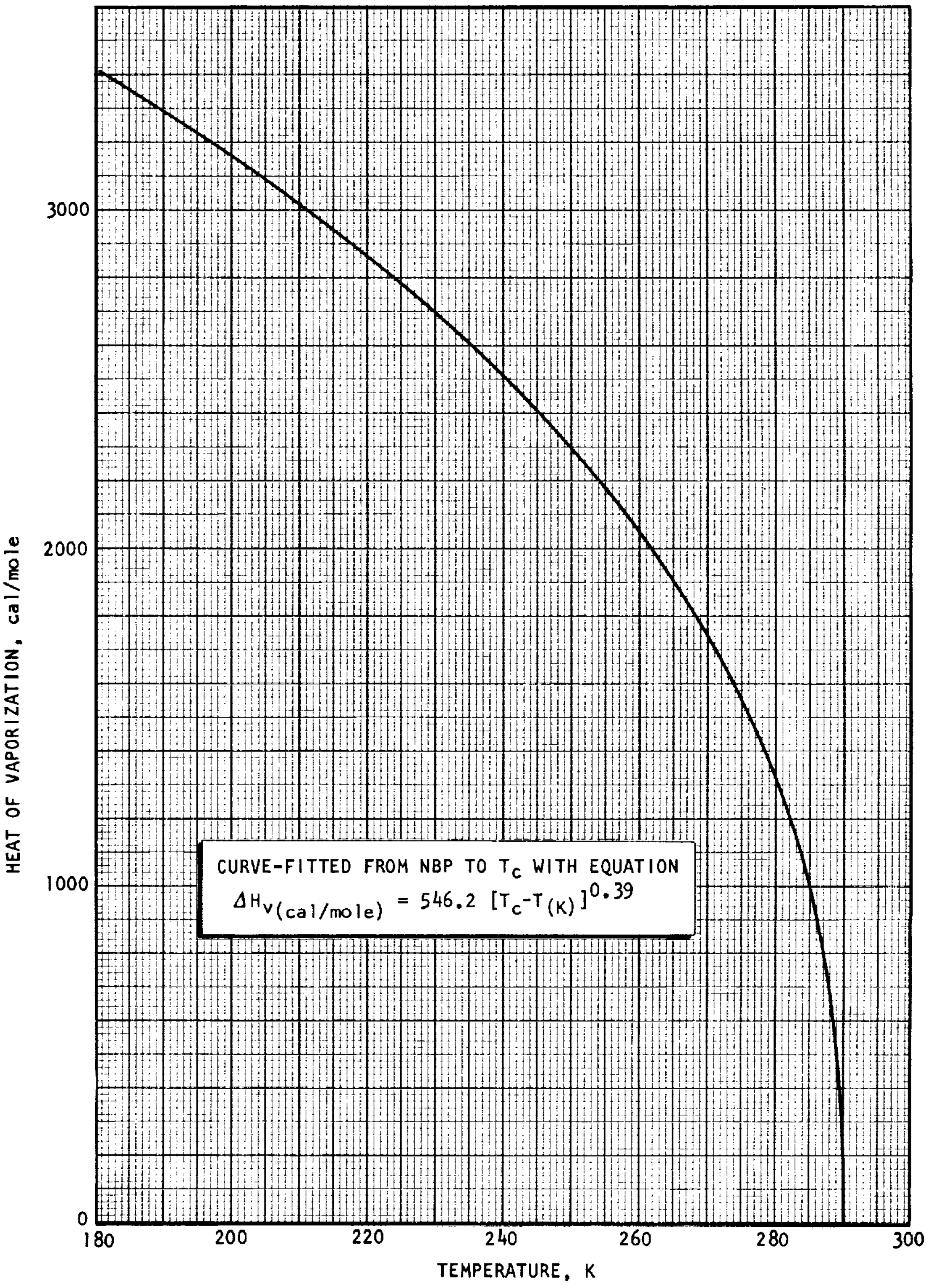


Figure 2.5. Heat of Vaporization of Diborane (Ref. 2.30)

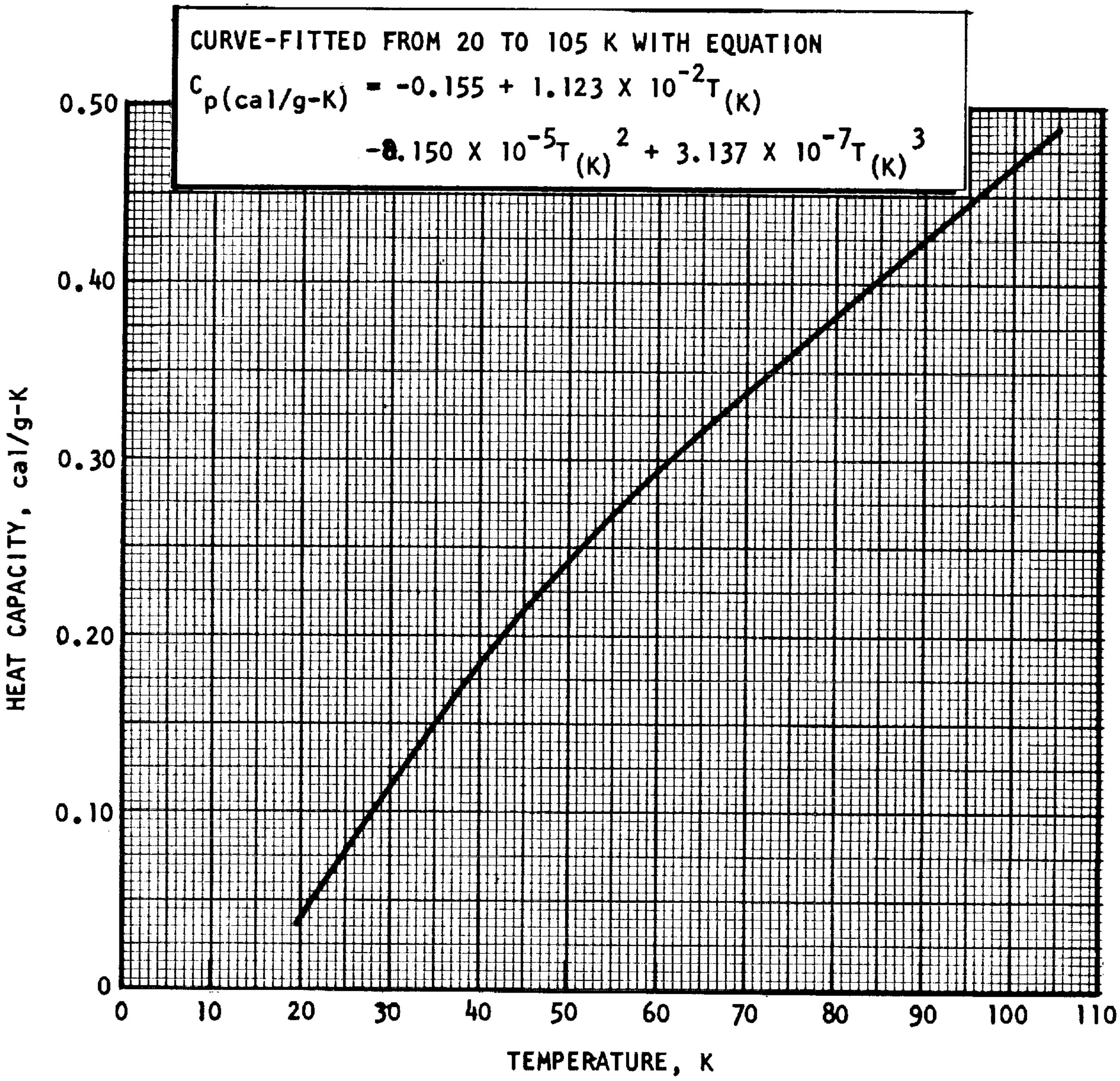


Figure 2.6. Heat Capacity of Solid Diborane (Correlated from Data of Ref. 2.3)

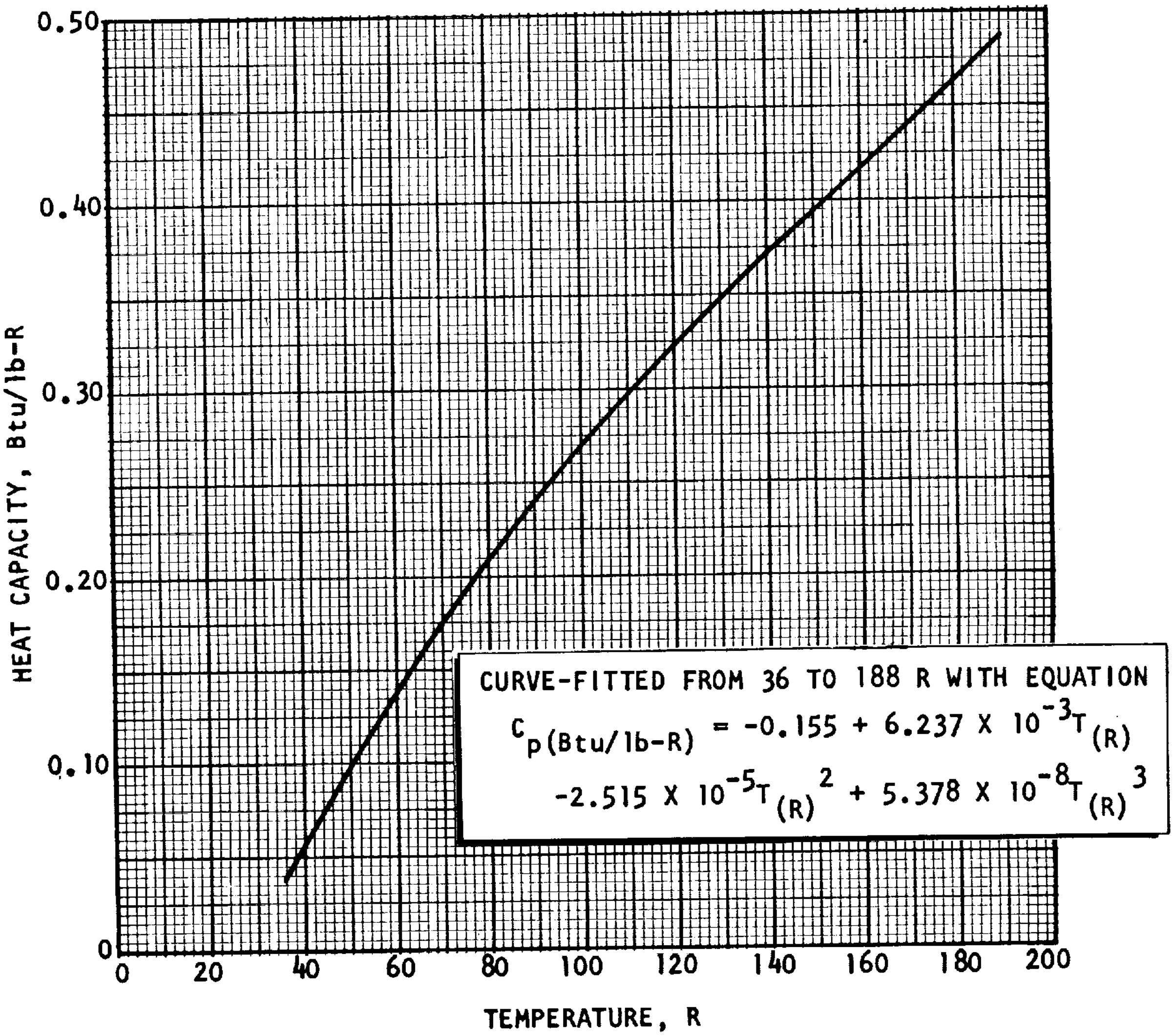


Figure 2.6a. Heat Capacity of Solid Diborane
(Correlated from Data of Ref. 2.3)

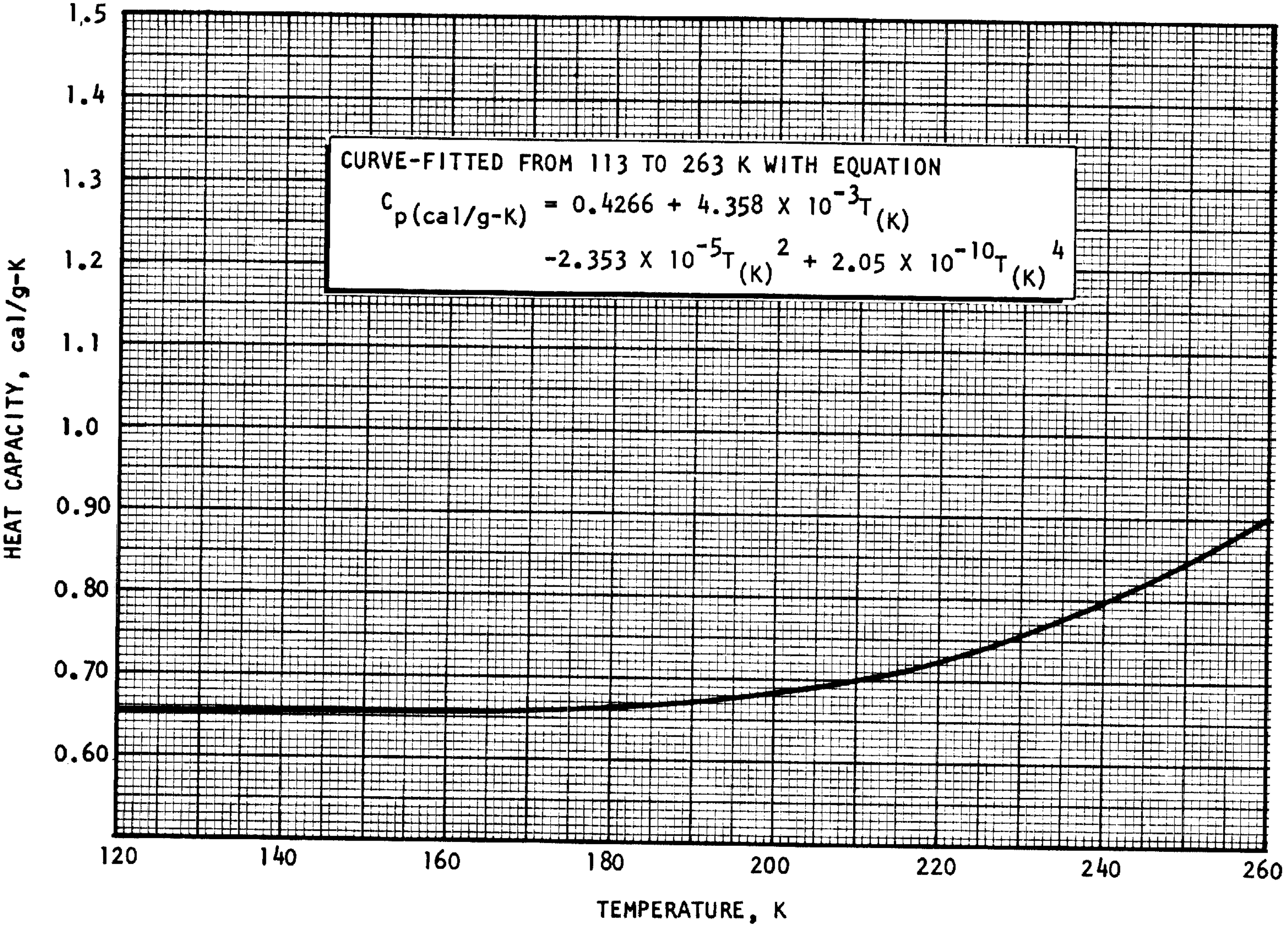


Figure 2.7. Heat Capacity of Saturated Liquid Diborane (Correlated from Data of Ref. 2.3 and 2.6)

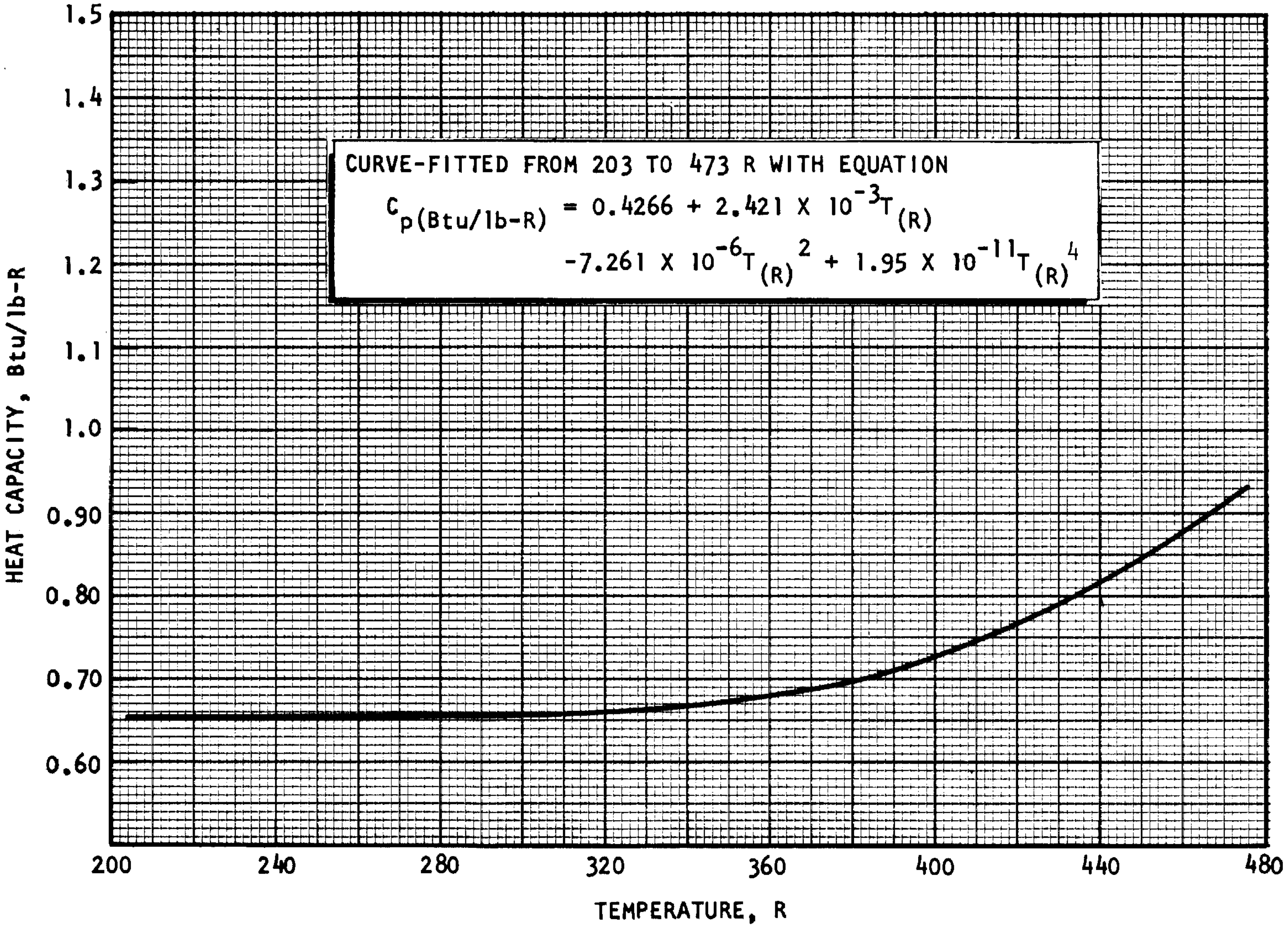


Figure 2.7a. Heat Capacity of Saturated Liquid Diborane (Correlated from Data of Ref. 2.3 and 2.6)

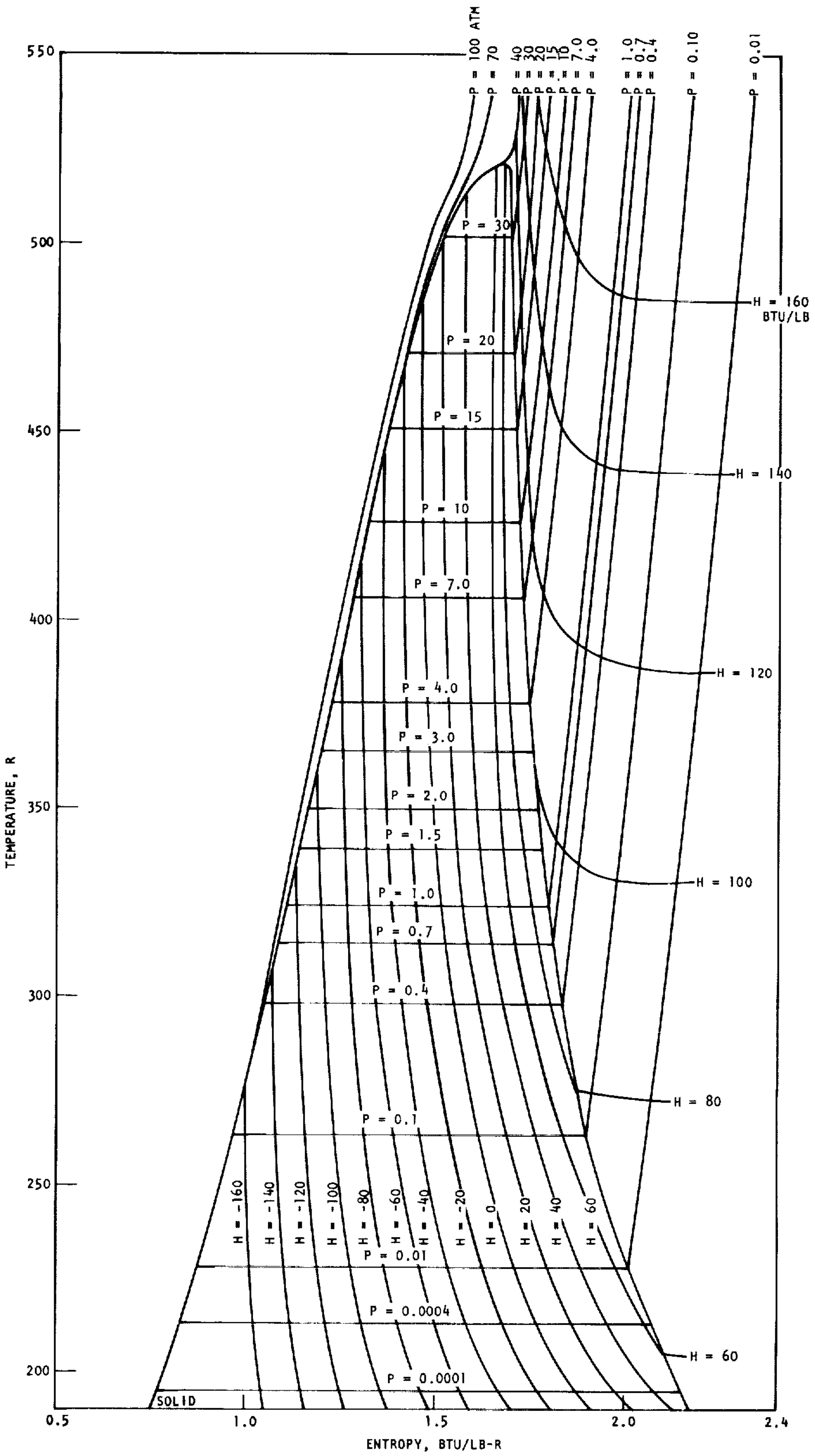


Figure 2.8. Temperature-Entropy Diagram for B_2H_6

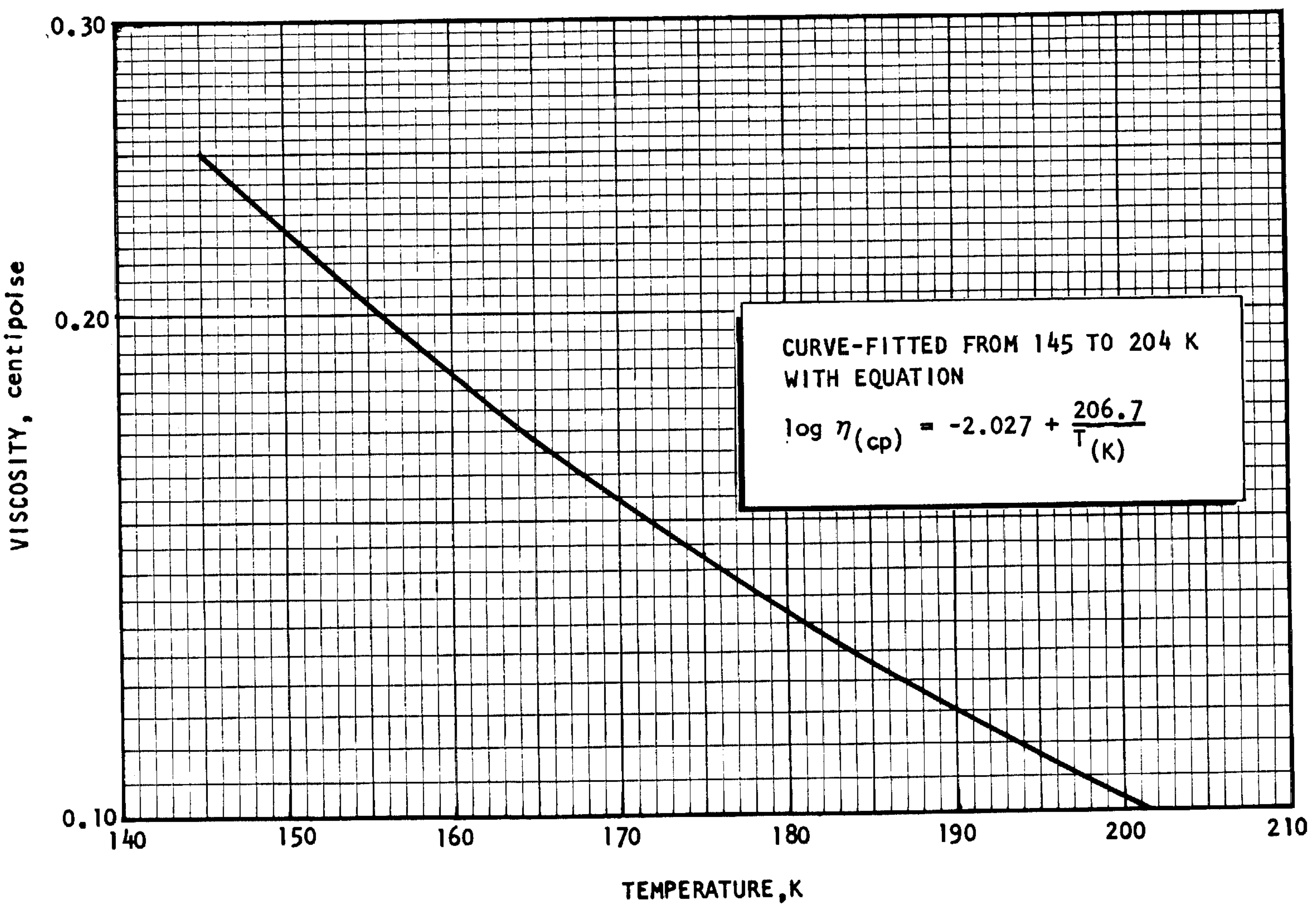


Figure 2.9. Viscosity of Liquid Diborane (Correlated from Data of Ref. 2.11)

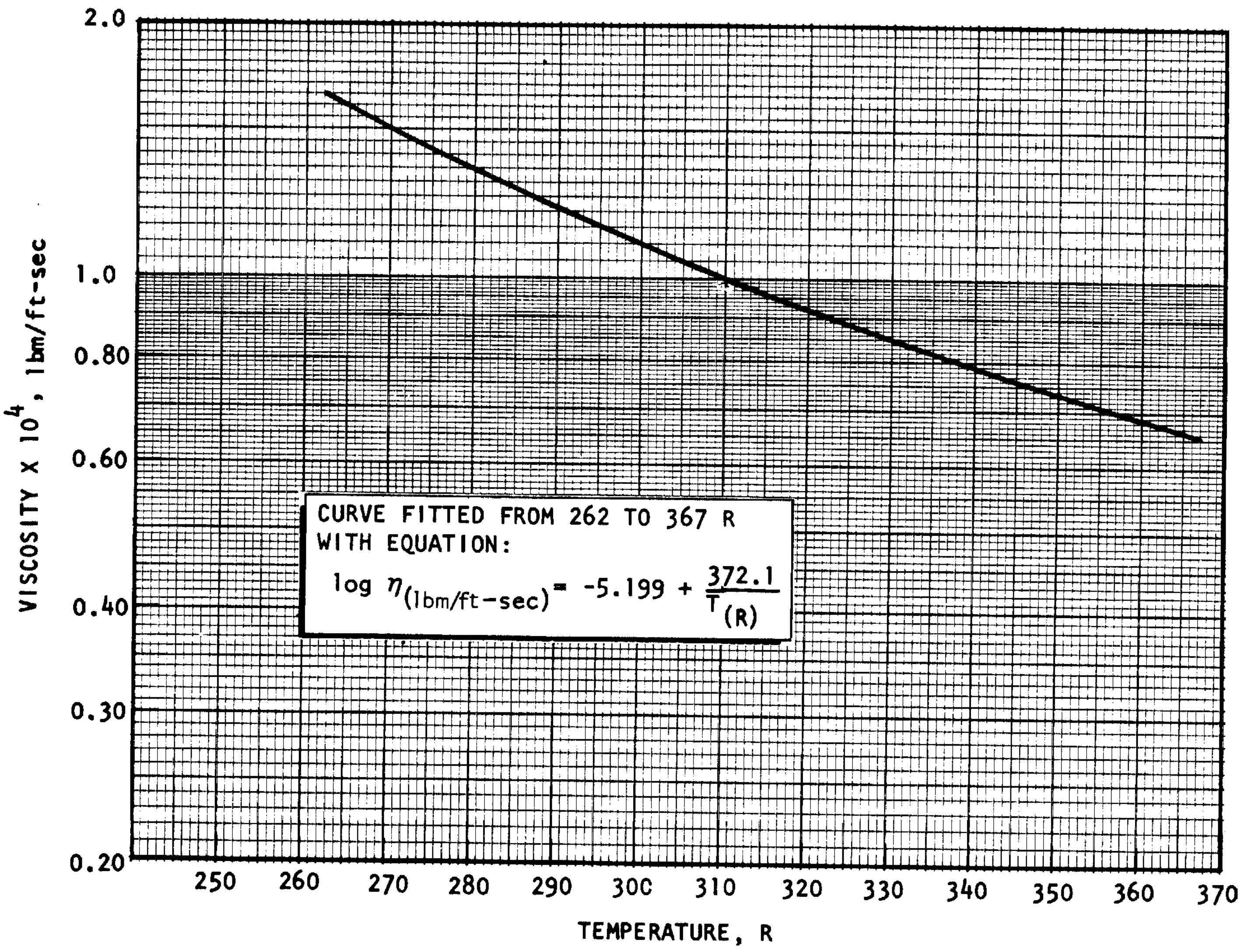


Figure 2.9a. Viscosity of Saturated Liquid Diborane (Correlated from Data of Ref. 2.11)

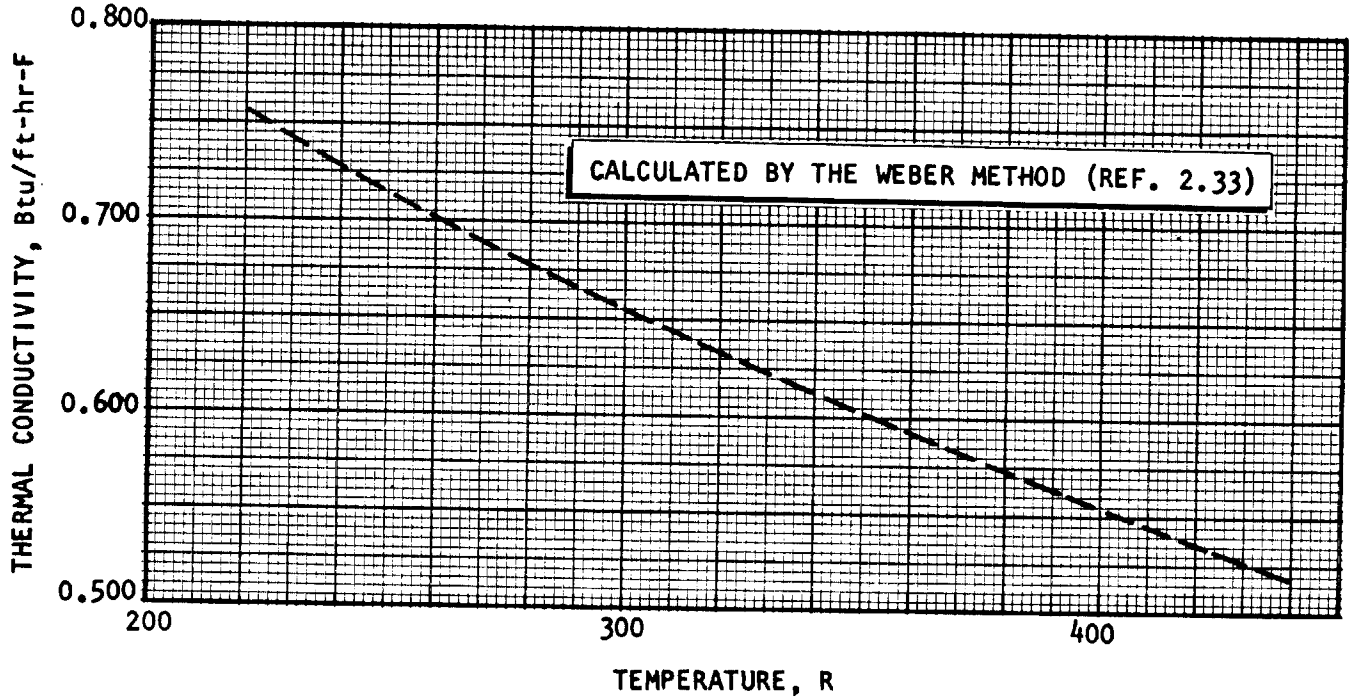


Figure 2.10. Thermal Conductivity of Liquid Diborane (Ref. 2.34)

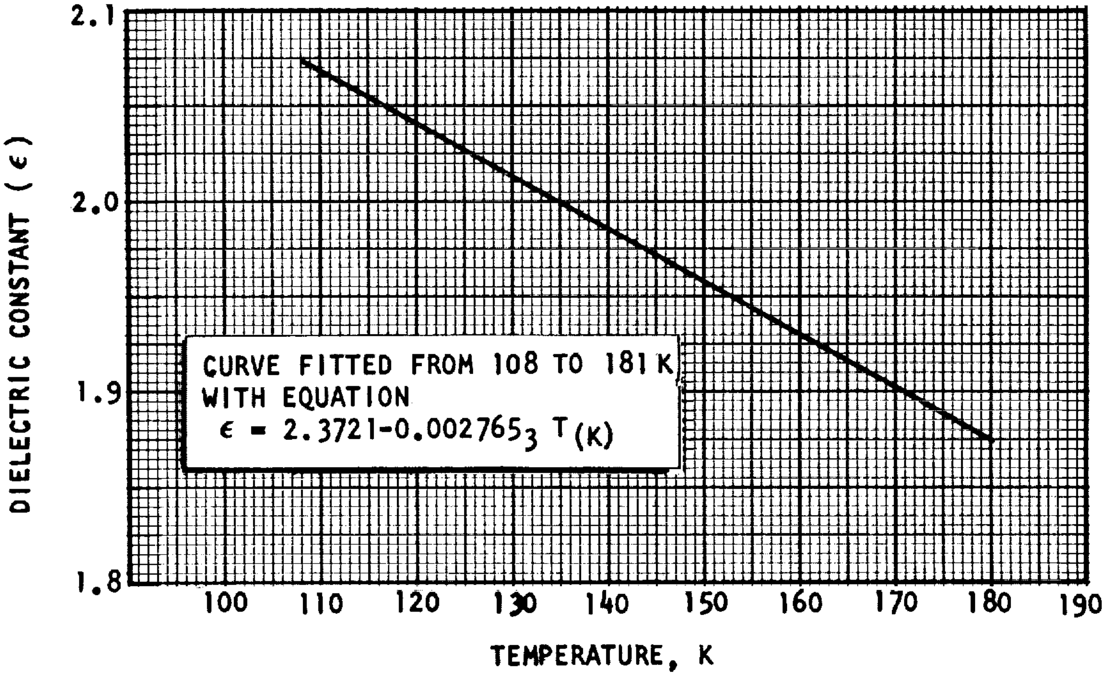


Figure 2.11. Dielectric Constant of Liquid Diborane (Ref. 2.4)

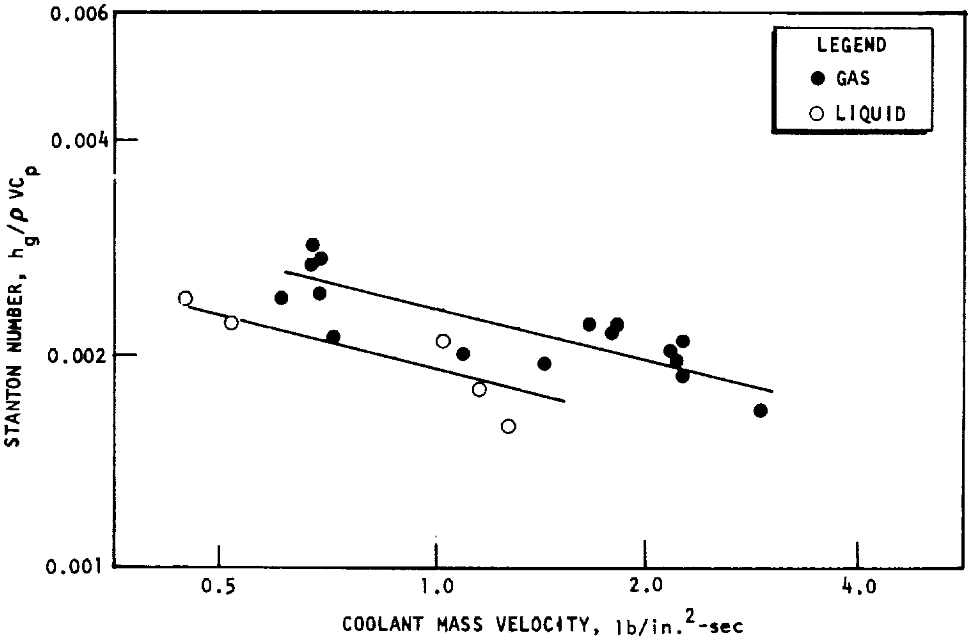


Figure 2.12. Stanton Number Correlation of B_2H_6 Heat Transfer (Ref. 2.119)

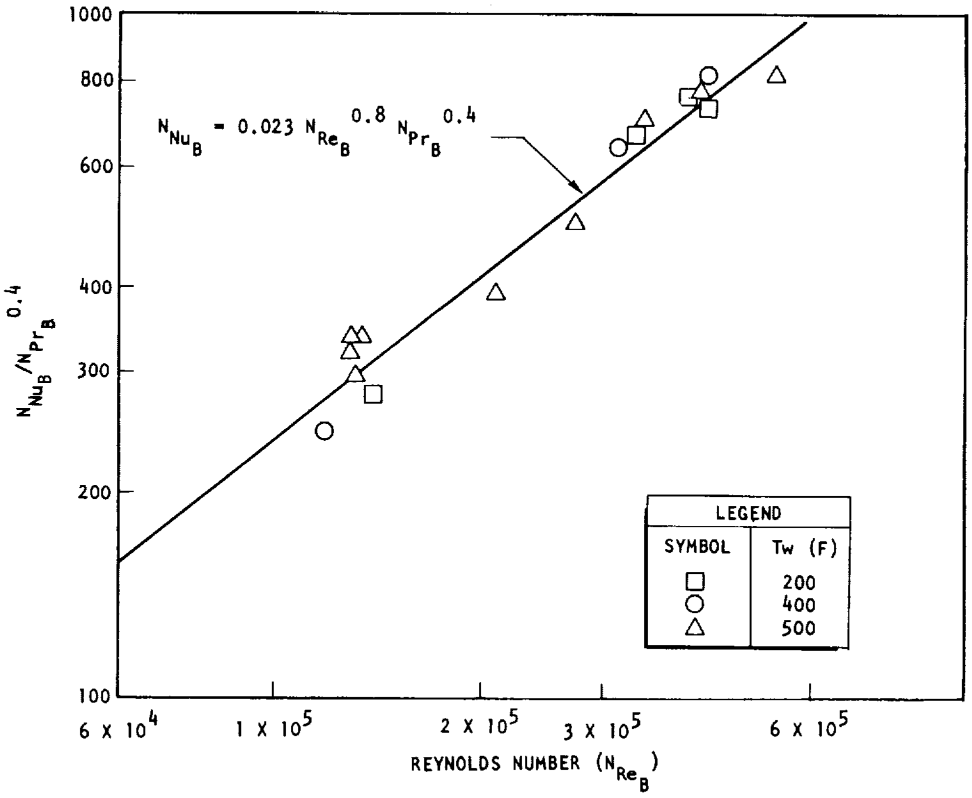


Figure 2.13. Nusselt Number Correlation of B_2H_6 Heat Transfer Data (Ref. 2.119)

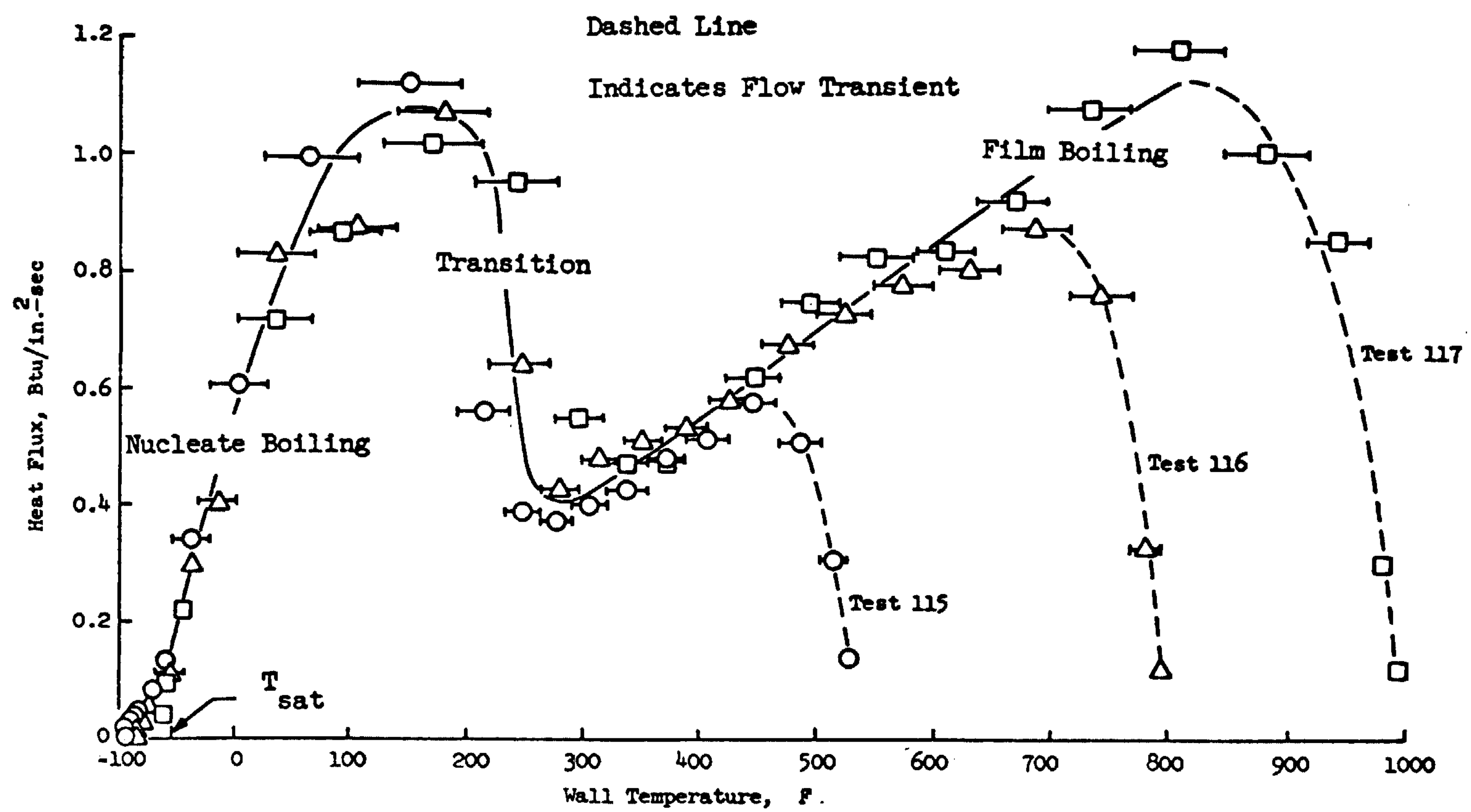


Figure 2.14. Injection Point Heat Transfer Without Decomposition (Reprinted from Ref. 2.119)

SECTION 3: PRODUCTION AND CHEMICAL ANALYSIS

3.1 MANUFACTURING TECHNIQUES

3.1.1 General Methods of Preparation

Diborane has been prepared in the laboratory and commercially by a large variety of processes. Although a number of reviews have been written on methods for the preparation of diborane, the most comprehensive are those presented by Adams, both chronologically (Ref. 3.1) and with respect to the processes employed (Ref. 3.2). General descriptions and information on the basic processes used for the preparation of diborane, its precursors, its intermediates, and its borane derivatives are also extensively summarized in Ref. 3.3. In addition, a composite of the processes for converting the ores of boron into diborane via their conversion to boron halides or sodium borohydride has been illustrated as a flow chart (redrawn as Fig. 3.1) in Ref. 3.4. Since complete summaries of the various processes for the general preparation of diborane are readily accessible in these reviews, the following discussion is directed briefly at some highlights in the development of the processes with direct applications to current commercial techniques.

Diborane was first isolated by Stock in 1912 (Ref. 3.5) from the pyrolysis product of tetraborane, prepared by acid hydrolysis of magnesium boride. In 1931, Schlesinger and Burg (Ref. 3.6) prepared diborane by passing hydrogen and boron trichloride through an electric discharge. Those methods are now of historic interest only. About 1944, the first essentially quantitative process for preparing diborane was developed by Schlesinger and Brown; it used lithium hydride to reduce boron trifluoride in diethyl ether (Ref. 3.7):

$$6\ \mathrm{LiH} + 8\ \mathrm{BF_3} \xrightarrow[\text{ether}]{} \mathrm{B_2H_6} + 6\ \mathrm{LiBF_4}$$

This method was used by Callery Chemical Company to prepare the first commercial quantities of diborane. Later, essentially the same method was successfully used in the General Electric pilot plant for diborane production (Ref. 3.8).

The intermediate in the LiH-BF_3 process is lithium borohydride. The lithium borohydride is soluble in either and reacts rapidly with boron halides to liberate diborane:

$$3\ LiBH_4 + 4\ BF_3 \xrightarrow[\text{ether}]{} 2\ B_2H_6 + 3\ LiBF_4$$

Subsequent efforts to improve methods of preparation of diborane focused on the more accessible sodium borohydride, $NaBH_4$. Eventually, the use of sodium borohydride was made feasible by the discovery of its solubility in the dimethyl ethers of the polyethylene glycols (Ref. 3.9). The preferred method became the reaction of sodium borohydride and boron trifluoride-ether complex in the dimethyl ether of diethylene glycol (diglyme):

$$3\ NaBH_4 + 4\ BF_3 \xrightarrow[\text{diglyme}]{} 2\ B_2H_6 + 3\ NaBF_4$$

Potassium borohydride was also used in place of the $NaBH_4$, and boron trichloride was employed to replace the BF_3.

A recent Czech patent (Ref. 3.10) claims that 99.5-percent yields of diborane are obtainable when sodium aluminum hydride, $NaAlH_4$, and BF_3-etherate are refluxed for 2 hours in monoglyme (ethylene glycol dimethyl ether).

Theoretically, the simplest and most direct route to diborane is the hydrogenation of boron:

$$2\ B + 3\ H_2 \longrightarrow B_2H_6$$

This route was vigorously pursued at Olin Mathieson Chemical Corporation by Clark et al., who patented processes for the production of B_2H_6 by passing hydrogen gas over boron with sulfur (Ref. 3.11) or boron with B_2O_3 (Ref. 3.12); however, required temperatures of around 1000 C (~1800 F) and low yields made these processes impractical for commercial applications. Enk and Nickl at Wacker-Chemic in Germany patented a process (Ref. 3.13) in which hydrogen is fed into an electrolyzed metal halide mixture with a boron anode; presumably, metal hydrides and boron halides are formed as intermediates, but the overall reaction is the hydrogenation of boron.

Many other approaches to the synthesis of B_2H_6 were studied, including those routes illustrated in Fig. 3.1, and numerous patents in this field have been issued (Ref. 3.2). The processes include electrolysis as well as catalytic and high-temperature treatments of various boron-containing compounds. Although interesting from a theoretical viewpoint, a great many of these processes are of limited practical utility. The present practical methods of the preparation of diborane are dominated by variants using borates, borohydrides (particularly $NaBH_4$), and/or the boron halides (BF_3 or BCl_3).

In addition to the commercial processes already discussed (i.e., the $LiH-BF_3$-ether and $NaBH_4-BF_3$-diglyme processes), other methods which have been used in pilot or production-scale plants include the reaction of an alkali metal hydride with methylborate; the reaction of an alkali metal with a boron halide; thermal hydrogenolysis of a boron halide; and thermal catalylic hydrogenolysis of a boron halide. These processes are discussed further in Section 3.1.3.

3.1.2 Small-Scale Generation of Diborane

Most of the physical and chemical characterization of diborane has been done on laboratory-prepared samples. However, basically, the commercial methods of manufacture of diborane are enlargements of the preferred laboratory methods. The present laboratory methods rely almost exclusively on sodium or potassium borohydrides as a source of diborane. Small-scale generation of diborane in a glass apparatus, for chemical experimentation (hydroboration in this case), is described in detail by Zweifel and Brown (Ref. 3.14). In this experimental apparatus, which is illustrated in Fig. 3.2, the B_2H_6 gas is generated by the dropwise addition of the sodium borohydride solution to the stirred boron trifluoride etherate-diglyme solution in a dry nitrogen atmosphere.

Other convenient methods for the small-scale generation of B_2H_6 are based on the general reaction

$$BH_4^- + H^+ \longrightarrow 1/2\ B_2H_6 + H_2$$

The borohydride ion is provided by either sodium or potassium borohydride, and the hydrogen ion by sulfuric acid, methanesulfonic acid, phosphoric acids, hydrogen chloride, or fluorinated acids (Ref. 3.2 and 3.15).

The method of Weiss and Shapiro (Ref. 3.16), often referred to in the literature, uses sodium borohydride and sulfuric acid. The one disadvantage of this otherwise convenient method is the presence of a large proportion of gaseous contaminants, particularly H_2S. This disadvantage is eliminated in a related method developed by Duke et al. (Ref. 3.17), which employs potassium borohydride and orthophosphoric acid. The presently recommended method of preparation of small quantities of pure diborane, described in Ref. 3.15, is a modification of Duke's procedure and uses potassium borohydride and 85-percent orthophosphoric acid, in a vacuum line. The reaction is

$$KBH_4 + H_3PO_4 \longrightarrow 1/2\ B_2H_6 + H_2 + K^+ + H_2PO_4^-$$

Because the laboratory storage of diborane gas often creates some problems, diborane is usually stored in the form of more stable liquid or solid adducts. For example, the pyridine adduct can be utilized for storage and purification; when needed for use, diborane can be displaced by treatment with BF_3. An even more convient way of storing diborane for laboratory use, as noted by Brown (Ref. 3.7), is the formation of sodium diborohydride, $NaBH_4$ BH_3 or NaB_2H_7:

$$NaBH_4 + 1/2\ B_2H_6 \rightleftharpoons NaB_2H_7$$

The reaction is reversible; at elevated temperatures, the diborane can be recovered.

3.1.3 Commercial Manufacture of Diborane

At the present, Callery Chemical Company is the only commercial manufacturer of diborane in the United States. However, four other companies have provided pilot- or production-scale quantities of diborane in the past. From 1946 to 1952, the General Electric Company operated a plant at Schenectady, New York to provide boranes (of which diborane is the key intermediate) for study as potential fuels for air-breathing aircraft engines. The Olin-Mathieson Chemical Corporation and the Callery Chemical Company, as a result of multimillion dollar contract awards in 1952 to develop the borane fuels, established large-scale production plants at Niagara Falls, New York and at Lawrence, Kansas and Muskogee, Oklahoma, respectively. Later contracts in 1957 provided the basis for the establishment of borane pilot plants by Stauffer-Aerojet Chemical Company (Richmond, California) and AFN (Los Angeles, California). By the middle 1960's, when the interest in the borane family of fuels declined, operations at all of these plants had ceased and borane production at Callery was limited to their Callery, Pennsylvania facility. Brief descriptions of the processes employed at all of these facilities are provided in the following paragraphs.

As noted previously in Section 3.1.1, the first commercial quantities of diborane were prepared by Callery Chemical Company using the LiH-BF_3 process (Ref. 3.1). After the work in glassware, a pilot plant was set up which used ether saturated with diborane to dissolve the

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lithium hydride. The solution was allowed to react with boron trifluoride-etherate. Yields of about 90 percent were obtained, with about 95-percent purity. The major impurity was ethane from some cleavage of the ether.

The General Electric pilot plant for diborane production by the $LiH\text{-}BF_3$ process has been described by Herrick et al. (Ref. 3.8). Diborane of 98-percent purity was prepared in 82.5-percent yield. However, Mikhailov (Ref. 3.18) in his review of the chemistry of diborane, considers the $LiH\text{-}BF_3$ method inferior, stating that "The assessment of this method as the simplest and the most economical for obtaining diborane is incorrect."

The process used by Callery production plants at Muskogee, Oklahoma and Lawrence, Kansas to produce diborane as a final product or intermediate in the production of other boranes involved the reaction of sodium hydride, NaH, with methylborate $(CH_3O)_3B$, via the following steps (Ref. 3.3):

$$H_3BO_3 + 4\ CH_3OH \xrightarrow{\text{distillation}} CH_3OH\cdot(CH_3O)_3B + 3\ H_2O \qquad (1)$$

$$CH_3OH\cdot(CH_3O)_3B \xrightarrow{\text{mineral oil extraction}} (CH_3O)_3B\text{(in mineral oil)} + CH_3OH \qquad (2)$$

$$2\ (CH_3O)_3B + NaH \xrightarrow{\text{in mineral oil}} (OCH_3)_2BH + NaB(OCH_3)_4 \qquad (3)$$

$$6\ (CH_3O)_2BH \rightleftharpoons B_2H_6 + 4\ (CH_3O)_3B \qquad (4)$$

Although the production plant conditions were not specified, a 98-percent yield of $(CH_3O)_3B$ was obtained in step 1; a 96-percent extraction of $(CH_3O)_3B$ was obtained with 99.9-percent purity recovered on distillation in step 2; a 94-percent yield of dimethoxyborane, $(OCH_3)_2BH$, was obtained in step 3 based on the NaH used; and the diproportionation of $(OCH_3)_2BH$ (step 4) resulted in nearly 100-percent conversion to diborane.

Callery has also employed the $NaBH_4$ - BH_3 - diglyme process for the commercial production of diborane in its Callery, Pennsylvania facility. A simplified flow sheet for a production plant using this process, given by Shepherd and Ayres of Callery Chemical Company (Ref. 3.19), is shown in Fig. 3.3. (Figures 3.2 and 3.3 represent a comparison of the laboratory and commercial production techniques in the use of this process.) In the production process, gaseous BF_3 is passed into a solution of $NaBH_4$ in pure, dry diglyme. During addition of the first half of the stoichiometric amount of BF_3, only a small amount of diborane is generated because of the formation of the complex $NaBH_4 \cdot BH_3$. To minimize thermal decomposition of the diborane, the temperature of the reaction mixture is maintained at 35 C by cooling and by adjusting the rate of addition. The diborane is passed into refrigerated condensers, liquefied, and allowed to run into storage cylinders. These are "topped" to remove residual hydrogen. The slurry of sodium tetrafluoroborate, $NaBF_4$, is filtered and the filtrate returned to a storage tank where makeup diglyme is added. In this plant, operations are carried out at slightly greater than atmospheric pressure. Because of the corrosive nature of BF_3 and by-products from the process, equipment and piping are made of stainless steel. Because of the flammability and toxicity of diborane, oxygen and moisture are rigorously excluded from the system. For safety, the equipment is designed for 150-psi working pressure, vents from the apparatus are discharged to methanol scrubbing towers, and nitrogen purges are used throughout.

In the Olin Mathieson production plant, diborane was produced by the reaction of lithium hydride, LiH, with boron trichloride, BCl_3, in the presence of diethyl ether, $(C_2H_5)_2O$, via the following steps (Ref. 3.3):

$$2\ B_2O_3 + 3\ C + 6\ Cl_2 \xrightarrow{(1100\text{-}1500\ F)} 4\ BCl_3 + 3\ CO_2 \qquad (1)$$

$$\text{or } 2\ B_2O_3 + 7\ C \longrightarrow B_4C + 6\ CO \qquad (1A)$$

$$B_4C + 6\ Cl_2 \longrightarrow 4\ BCl_3 + C \qquad (1B)$$

$$2\ BCl_3 + 6\ LiH \xrightarrow{(C_2H_5)_2O} B_2H_6 + 6\ LiCl \qquad (2)$$

or $$2\ BCl_3 + 2\ (C_2H_5)_2O \longrightarrow 2\ BCl_3 \cdot O(C_2H_5)_2 \qquad (2A)$$

$$6\ LiH + 3\ B_2H_6 \longrightarrow 6\ LiBH_4 \qquad (2B)$$

$$6\ LiBH_4 + 6\ (C_2H_5)_2O \longrightarrow 6\ LiBH_4 \cdot O(C_2H_5)_2 \qquad (2C)$$

$$6\ LiBH_4 \cdot O(C_2H_5)_2 + 2\ BCl_3 \cdot O(C_2H_5)_2 \longrightarrow 4\ B_2H_6 + 6\ LiCl + 8\ (C_2H_5)_2O \qquad (2D)$$

It was claimed that all reactions in the second step (steps 2A through 2D) were essentially 100-percent complete with very slight side reactions. The reactions 2A, 2C, and 2D are rapid while reaction 2B is slow.

The Stauffer-Aerojet pilot plant utilized the thermal hydrogenolysis of boron trichloride, BCl_3 to prepare diborane via the following steps (Ref. 3.3):

$$Na_2B_4O_7 + 8\ C \xrightarrow{1832\ F} B_4C + 7\ CO + 2\ Na \qquad (1)$$

$$B_4C + 12\ HCl \longrightarrow 4\ BCl_3 + 6\ H_2 + C \qquad (2)$$

$$BCl_3 + H_2 \xrightleftharpoons{1742\ F} BHCl_2 + HCl \qquad (2A)$$

$$6\ BHCl_2 \longrightarrow B_2H_6 + 4\ BCl_3 \qquad (3)$$

Yields from the carbothermal reduction of sodium tetraborate, $Na_2B_4O_7$, (step 1) varied from 45 to 66 percent based on $Na_2B_4O_7$; chlorination of boron carbide, B_4C, with hydrogen chloride, HCl, resulted in a 55-percent yield of the equilibrium to BCl_3 per pass, and almost complete conversion on recycle; the reaction of BCl_3 with H_2, quenched

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at 200 C (392 F) to prevent the back reaction, resulted in a 77-percent yield of dichloroborane, $HBCl_2$; and the disproportionation of $HBCl_2$ to diborane gave a 100-percent yield at 74 C (165 F) and 85 psig.

The AFN (American Potash, Food Machinery, and National Distillers, Inc.) pilot plant utilized the thermal catalytic hydrogenolysis of BCl_3 in the preparation of diborane via the following steps (Ref. 3.3):

$$Na_2B_4O_7 + H_2SO_4 + 5\ H_2O \longrightarrow 4\ H_3BO_3 + Na_2SO_4$$

or (1)

$$Ca_2B_6O_{11} + 2\ H_2SO_4 + 7\ H_2O \longrightarrow 6\ H_3BO_3 + 2\ CaSO_4$$

$$2\ H_3BO_3 \xrightarrow{heat} B_2O_3 + 3\ H_2O \qquad (2)$$

$$2\ B_2O_3 + 3\ C + 6\ Cl_2 \xrightarrow{(>1200\ F)} 4\ BCl_3 + 3\ CO_2 \qquad (3)$$

$$6\ BCl_3 + 6\ H_2 \rightleftharpoons 6\ HBCl_2 + 6\ HCl \qquad (4)$$

$$6\ HBCl_2 \rightleftharpoons B_2H_6 + 4\ BCl_3 \qquad (5)$$

An overall yield of 99.4 percent was claimed for the preparation of $HBCl_2$ (step 4), while an overall yield of 65.5 percent based on $HBCl_2$ was obtained in the disproportionation step (5).

The optimum process currently used by the Callery Chemical Company to manufacture diborane is proprietary, although they still employ both the alkali metal hydride-methylborate and the $NaBH_4$-BF_3-diglyme processes, depending on the production quantities desired. If the production demand ever necessitates the reactivation of the Lawrence, Kansas plant, the basic production technique will follow the alkali metal hydride-methylborate process.

3.1.4 Separation and Purification of Diborane

In earlier methods of synthesis, the yields were so low that diborane could be regarded as a by-product. New methods of synthesis are nearly quantitative but the product still contains various contaminants. After separation and plant purification, commerical diborane is nominally 95-percent pure. The major volatile impurities are hydrogen and hydrocarbons; there are also traces of other contaminants. Hydrocarbons originate from cleavage of the solvent, while halogen impurities come from the boron halide used. During storage of diborane, some amounts of higher boron hydrides are formed (particularly if the storage temperature approaches room temperature); these hydrides accelerate further decomposition of diborane.

The most economical separation of large quantities of diborane from higher hydrides, and most of its other impurities, is done by fractional distillation. Impure diborane is passed through a cold trap, usually at -126 C (-194.8 F), prior to collection at liquid nitrogen temperatures:

$$\begin{array}{l}\text{Mixed boranes,}\\ \text{impure diborane}\end{array} \xrightarrow[(-195\ \text{F})]{-126\ \text{C}} \begin{array}{l}B_2H_6 \text{ passes through,}\\ \text{higher boranes}\\ \text{condense}\end{array} \xrightarrow[(-320\ \text{F})]{-196\ \text{C}} \begin{array}{l}B_2H_6\\ \text{condenses}\end{array}$$

Cold baths used in fractional distillation of diborane are LN_2-carbon disulfide slush (-111.6 C or -168.9 F), LN_2-methylcyclohexane slush (-126 C or -195 F), and LN_2-n-pentane slush (-130 C or -202 F). The purity of B_2H_6 can be conveniently checked by the measurement of its vapor pressure (225 mm at -111.6 C).

However, Duke et al. (Ref. 3.17) indicated that when diborane is prepared by the Weiss and Shapiro method, i.e., from $NaBH_4$ and sulfuric acid, the product contaminants (mainly H_2S and CO_2) are difficult to remove by fractional distillation because the vapor pressures of B_2H_6, H_2S, and CO_2 at -126 C are 70 mm, 6 mm, and 5 mm, respectively.

Diborane can be freed from ethane and similar impurities by the technique of conversion into a pyridine (C_5H_5N) complex and subsequent liberation with BF_3:

$$2\ C_5H_5N + B_2H_6\ \text{(impure)} \longrightarrow 2\ C_5H_5N\cdot BH_3$$

$$2\ C_5H_5N\cdot BH_3 + 2\ BF_3 \longrightarrow B_2H_6\ \text{(pure)} + 2\ C_5H_5N\cdot BF_3$$

This method was patented by Schaeffer and Barbaras (Ref. 3.20). The pyridine-borane complex melts at 10 to 11 C (50 to 52 F), and has a vapor pressure of 0.1 mm at 25 C (Ref. 3.19).

A number of procedures for separating and purifying diborane from other specific contaminants have been developed. Diborane can be freed from ether by passage through aluminum chloride (Ref. 3.2). Purification of B_2H_6 from acid contaminants is effected by bringing the mixture in contact with $NaBH_4$ in diglyme, as patented by Huff (Ref. 3.21). Diborane can be separated from halogenated hydracids by the treatment with tricresyl phosphate (Ref. 3.22). Cueilleron and Bouix (Ref. 3.23) investigated purification of diborane by complex formation with ether-oxides, and by selective adsorption on synthetic zeolites.

Gas chromatography has also been used to separate various compounds from diborane (Ref. 3.24 through 3.26). Gorbunov in Russia (Ref. 3.25) used a column with tricresyl phosphate on porous glass or Celite.

A different approach, separation of diborane from gas mixtures by means of a permeable membrane, was studied and patented early by Birdwhistel et al. at Olin Mathieson Chemical Corporation (Ref. 3.27). They found that the diborane diffuses through methyl silicone rubber twice as fast as hydrogen, and 4 to 5 times as fast as nitrogen.

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3.2 CURRENT PRODUCTION

3.2.1 Availability

Liquid diborane is currently available from Callery Chemical Company (Callery, Pennsylvania 16024, Attn: A. J. Toering), the only present commercial manufacturer and supplier. Very small amounts of gaseous B_2H_6 can be obtained from other suppliers (e.g., Matheson Company, Atomergic Chemetals, Ventron Corporation, etc.); however, these are only available as ppm in mixtures with inert gases.

The current production capacity of the Callery plant is 20 to 25,000 pounds/year (Ref. 3.28). For production orders within this capacity, only a minimum lead time is required. If larger quantities are required over extended periods, Callery would reactivate their Lawrence, Kansas production plant. (The Muskogee, Oklahoma plant, which was a government-owned facility capable of producing 6 tons of diborane per day, was declared surplus several years ago.) The potential supply of diborane from other companies is unknown; however, all other previous commercial manufacturers of diborane have indicated their production plants have been disassembled.

3.2.2 Cost

The current price of liquid B_2H_6 depends on the amount of material required. Prices currently quoted by Callery (Ref. 3.28) are as follows:

B_2H_6 Quantity, pounds	Price per Pound, dollars
100 (grams)	80.00 (per 100 grams)
1	180.00
5	100.00
20 to 40	85.00

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The cost of larger quantities are based on increased production rates as follows (Ref. 3.28):

B_2H_6 Production, pounds/month	Price per Pound, dollars
500	75.00
2,000	65.00
5,000	35.00
10,000	15.00 to 20.00
20,000	10.00 to 15.00
1,000,000	3.50 to 5.00 (projected)

Since the cost of diborane can fluxuate widely depending on the total demand, the above costs represent only an order-of-magnitude price for advanced planning purposes; the manufacturer or supplier should be contacted for current quotations to meet known detailed requirements.

3.3 CHEMICAL ANALYSIS

Because diborane is extremely toxic and very reactive towards a number of chemicals, including air and moisture, one of the most important considerations in chemical analysis of diborane is sampling technique and sample handling. Proper handling of the sample is required to prevent sample degradation and provide reliable analysis of propellant quality. Although handling considerations are discussed more extensively in Section 4.5, two of the more important considerations are briefly noted here as a reminder in handling of a sample during sampling and chemical analysis.

Sample transfers should be made in a well-ventilated area and in perfectly clean, dry, and air-tight apparatus. In the laboratory, diborane sample transfers are normally made in dry boxes. Another property of diborane which tends to degrade the product is its tendency to form higher molecular weight boron hydrides as the temperature rises (see Section 4.1); therefore, samples should be maintained as a liquid (i.e., dry ice temperatures) or below room temperature until they are analyzed. They should not be exposed to room temperatures for more than 1 hour prior to analysis (Ref. 3.29).

The available analytical methods for diborane fall into two general classes: (1) assay methods, and (2) methods for the determination of other impurities. The assay methods include instrumental techniques, such as mass spectrometry, infrared spectrophotometry, and gas chromatography, as well as chemical analysis by a gas evolution technique. In addition, physical property measurements are employed as semi-qualitative evaluations of diborane purity.

There does not seem to be any consensus uniformity in the procedures used for total chemical analysis of diborane. In many cases, the analysis technique is determined by the particular test the propellant is undergoing. In a recent study to determine the potential existence of small amounts of impurities in diborane, TRW Systems Group (Ref. 3.30) assayed diborane by mass spectrometry and determined particulate formation by changes in Tyndall effect. In recent studies at Rocketdyne to pinpoint flow problems, diborane was assayed chemically by a hydrogen evolution technique and nonvolatile residue determined by controlled evaporation in a closed system. Olin Mathieson (Ref. 3.31) reports that high-purity samples are best analyzed by use of infrared spectrometric and gas chromatographic techniques. Callery (Ref. 3.29) reports on several assay methods but gives details on the hydrogen evolution and boron analysis procedure, indicating a preference for this approach.

3.3.1 Propellant Assay

3.3.1.1 Hydrogen Evolution on Hydrolysis, and Boron Analysis. The hydrolysis method is based upon the reaction of the diborane with excess methanol at low temperatures to yield hydrogen and methyl borate:

$$B_2H_6 + 6\ CH_3OH \longrightarrow 6\ H_2 + 2\ B(OCH_3)_3$$

The methylborate is hydrolyzed to boric acid by addition of water or dilute hydrochloric acid solution and the boric acid titrated by the standard mannitol method (Ref. 3.32).

Rocketdyne combines the hydrolysis steps in the following manner: a known quantity of a representative sample is frozen into a reaction vessel cooled to -196 C (-320 F). Hydrochloric acid (4 N) in 25-percent methanol is added and the flask allowed to warm slowly, first to -78 C (-108 F), then to room temperature. The flask is then cooled to -196 C (-320 F) and the hydrogen pumped (using a Toepler pump) into a calibrated volume. The warming, cooling, and pumping steps are repeated several times. The quantity of hydrogen is then determined by P-V-T measurements, i.e.,

$$\frac{P_2V_2T_1}{P_1V_1T_2} = y$$

where y is millimoles of hydrogen/millimole of sample

P_1, T_1, and V_1 are the pressure, temperature, and volume of the diborane sample

P_2, T_2, and V_2 are the pressure, temperature, and volume of hydrogen

From this

$$\text{percent diborane} = \frac{100\ y}{6}$$

The hydrolysate is then analyzed for boric acid by the mannitol method.

3.3.1.2 Mass Spectrometry. Analysis of diborane by mass spectrometry gives a complete analysis, including impurities, of all volatile species. However, it requires calibration with samples containing known diborane and impurity compositions. In addition, extreme care in avoiding decomposition or contamination in the instrument inlet system must be exercised. Traces of water adsorbed on the walls of the inlet system will yield high hydrogen results.

The sample is introduced to the instrument through vacuum-tight connections. Representative liquid samples may be obtained by inverting a sampler directly onto the inlet and bleeding a liquid sample into the inlet or by obtaining a representative gas sample on a vacuum line. Mass numbers 2 to 100 are scanned.

A typical mass cracking pattern of diborane is shown in Table 3.1 (taken from Ref. 3.29).

3.3.1.3 Infrared Spectrophotometry. The infrared absorption spectrum of pure diborane has been determined (Ref. 3.33) with a double-beam Perkin Elmer Model 21, Serial No. 161, equipped with a sodium chloride prism. It was possible to fill a 5.00-cm Baird-type gas cell and obtain a spectrum (from 2 to 15 microns) within 0.5 hours during which time decomposition was negligible. The absorption spectrum for a 5.00-cm path length is shown in Fig. 3.4.

3.3.1.4 Gas Chromatography. Gas chromatography methods for the determination of diborane and its impurities are based on several approaches reported in Ref. 3.24 through 3.26 and 3.34. Selection of a particular technique is largely dependent on the possible impurities; diborane can be separated from the higher boranes (Ref. 3.34), hydrogen (Ref. 3.26 and 3.34), ethane (Ref. 3.34), chloroboranes (Ref. 3.26), and hydrogen chloride (Ref. 3.26).

3.3.1.5 Physical Properties Measurements. The purity of diborane can also be qualitatively confirmed by measurement of its vapor pressure (given in Section 2.2.2.4). A convenient temperature level for this determination is -111.6 C (-168.9 F), the temperature of a LN_2-carbon disulfide slush bath, where the vapor pressure of pure diborane is 225 mm or 4.35 psia (Ref. 3.31). In addition, a molecular weight determination is frequently used at Rocketdyne to confirm purity. Approximately 1 millimole of gas is accurately weighed in a thin-walled 100-ml glass container, and the pressure and temperature measured to calculate molecular weight.

3.3.2 Other Impurities

In addition to use of the mass spectrometric and gas chromatographic techniques to determine diborane impurities, nonvolatile residues, particulates, and higher boron hydrides can be determined by the following techniques.

3.3.2.1 Nonvolatile Residue. Nonvolatile residue is determined gravimetrically in a specially constructed Kel-F apparatus which allows introduction of a known amount of liquid (15 ml) and subsequent controlled distillation of the diborane. The 15-ml sample is frozen into the Kel-F thimble at -196 C (-320 F). A -196 C bath is put on a receiver and the Kel-F thimble warmed slowly to room temperature and then weighed.

3.3.2.2 Particulates. Diborane has been analyzed for the presence of particulates after storage by examining it at temperatures near the storage temperature (Ref. 3.20). The liquid is examined for evidence of, and changes in, Tyndall effect during temperature cycling by measuring the scattered light at right angles to the incident beam passing through the liquid. This procedure determines if colloidal impurities are present or insoluble impurities deposited during cycling. A laser light source was used in these studies to maximize detection sensitivity.

3.3.2.3 Higher Boron Hydrides. The infrared absorption spectra of diborane may also be used for qualitative identification of higher boron hydride impurities. However, infrared inactive materials, such as hydrogen and nitrogen, are not detectable. The infrared absorption curve for B_2H_6 (see Fig. 3.4) and other boron hydrides can be found in Ref. 3.33.

3.3.3 Typical Analysis

Typical chemical analyses of samples taken from diborane production lots and diborane storage cylinders stored at -20 C for 1 year are given in Tables 3.2 and 3.3.

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3.4 PROPELLANT SPECIFICATION

At present, there are no military, manufacturing, or industrial specifications for diborane. The diborane currently produced by Callery is guaranteed to be at least 96-percent B_2H_6, but is typically 99+ percent (Ref. 3.28).

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TABLE 3.1

MASS SPECTRUM OF DIBORANE*

Typical Mass Spectrum Obtained using a Consolidated Electrodynamics 21-103 C Mass Spectrometer (ionizing voltage = 70; tungsten filament; ambient temperature inlet)

Mass No.	Relative Intensity	Mass No.	Relative Intensity
2	2.67	22	10.67
10	6.32	23	46.19
11	25.72	24	88.88
11.5	0.41	25	55.02
12	16.51	26	100
13	24.05	27	99.60
20	0.20	28	0.22
21	3.41		

*Ref. 3.29

TABLE 3.2

TYPICAL CHEMICAL ANALYSIS OF DIBORANE PRODUCTION LOT (REF. 3.31)

Diborane Assay	99+ mole percent
Impurities	trace C_2H_6

TABLE 3.3

CHEMICAL ANALYSIS OF DIBORANE AFTER ONE-YEAR SHIPPING CYLINDER STORAGE AT -20 C (Ref. 3.30)

Constituent	Mole Percent
Diborane Assay	94.5
Hydrogen	3.6
Nitrogen	0.31
Oxygen	0.00
Hydrocarbons (as Butene)	0.79
Carbon Dioxide	0.10
Isopropoxypentaborane	0.64

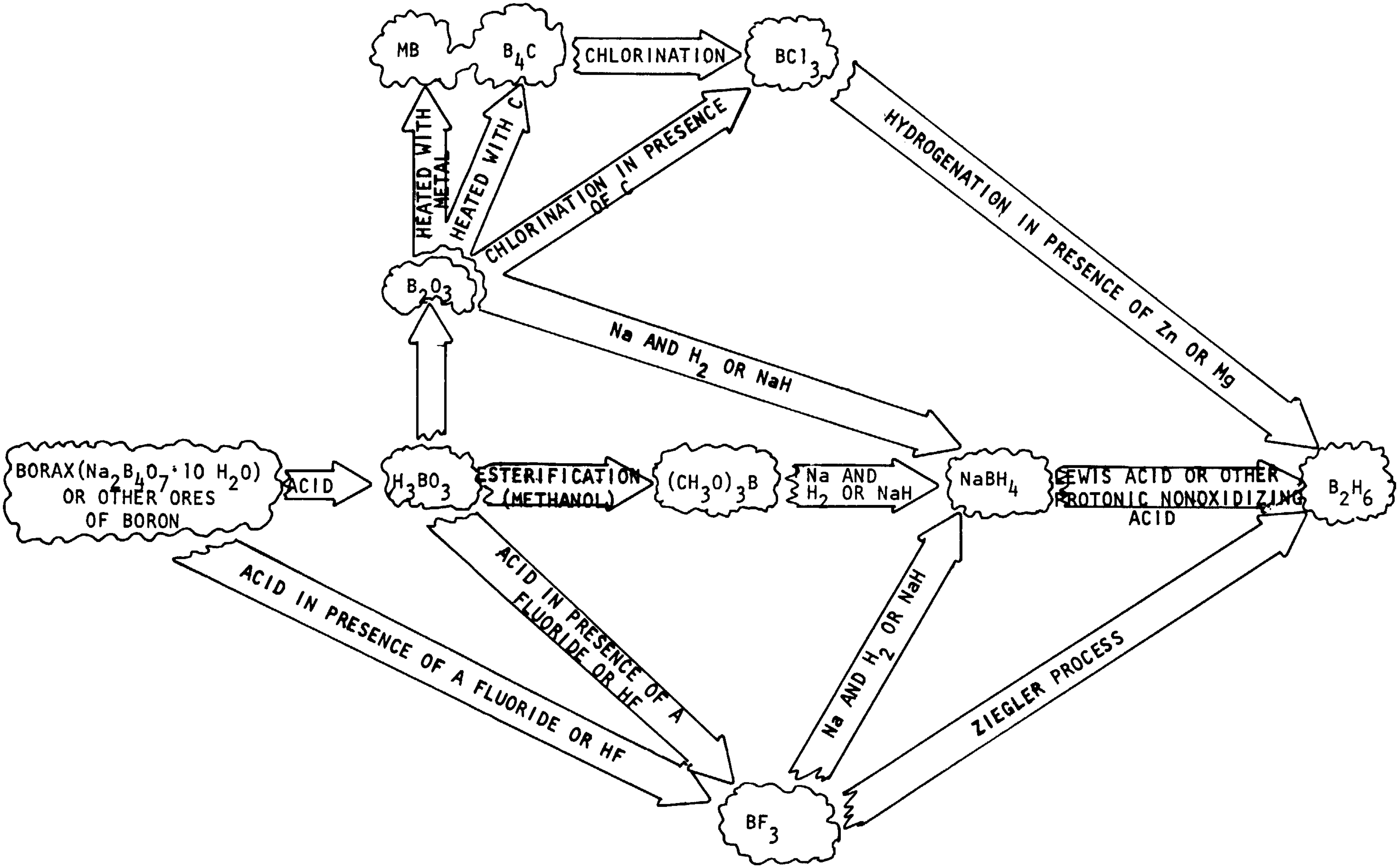

Figure 3.1. Flow Chart for the Preparation of Diborane via the Conversion of Boron Ores Into Boron Halides or Sodium Borohydride (Ref. 3.4)

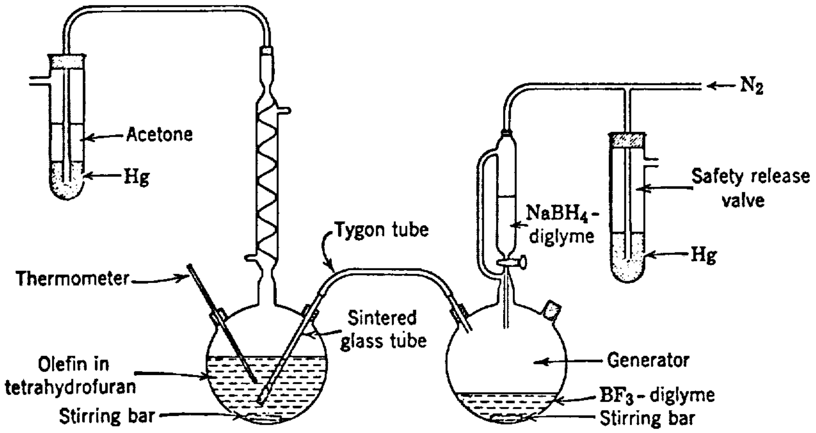

Figure 3.2. Laboratory Method for the Preparation of Diborane (Ref. 3.14)

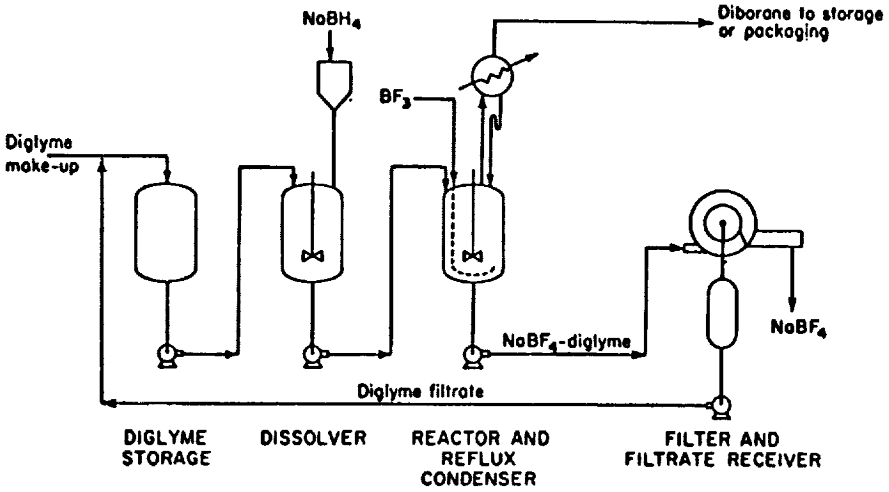

Figure 3.3. Flow Diagram for the Commercial Manufacture of Diborane by the $NaBH_4$-BF_3-Diglyme Process (Ref. 3.19)

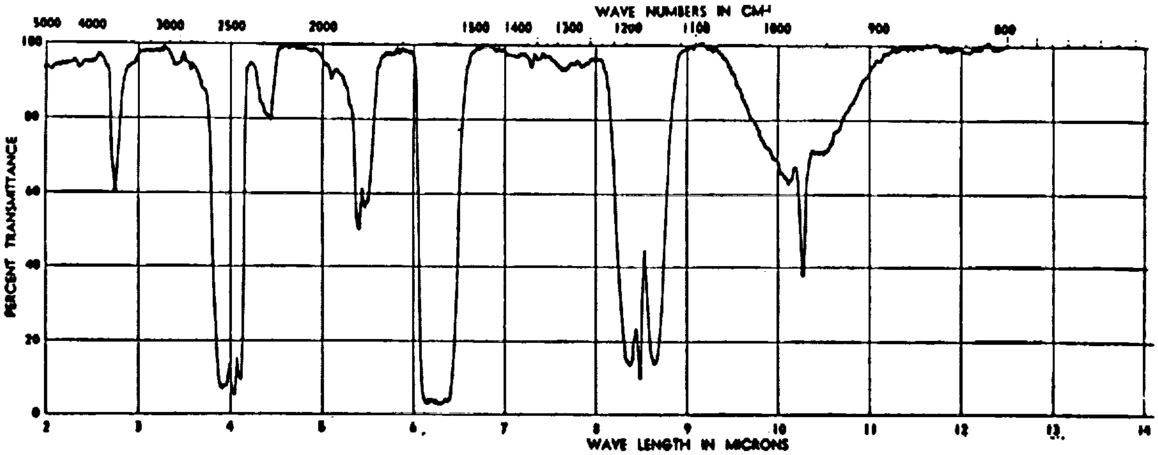

Figure 3.4. Infrared Absorption Curve of Diborane, B_2H_6, Obtained on Baird Double-Beam Spectrophotometer at 100.1 mm and 25 C (Ref. 3.33)

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SECTION 4: STORAGE AND HANDLING

4.1 STORABILITY

Although there is a distinct requirement for additional storage and thermal stability data on B_2H_6, the presently available data indicate that B_2H_6 can be stored safely without excessive decomposition as a liquid or cold gas at temperatures $\leq$ -20 C (-4 F) for extended periods of time (Ref. 4.1). In addition, its minimum storage life has been noted (Ref. 4.2) as > 14 months at -108 F (-78 C). These statements assume that the B_2H_6 storage system is fabricated from compatible materials, properly cleaned and passivated, and maintained free from moisture, oxygen, and other contamination.

Thus, as indicated above, the storability (or storage stability) of B_2H_6 is related primarily to its decomposition rate as a function of temperature (and possibly contacting materials) and its reactivity with moisture and oxygen. The nature of the B_2H_6 sensitivity to oxidation, hydrolysis, and other types of contamination that are frequently introduced inadvertently into propellant storage and handling systems is well recognized (see Sections 2.3 and 6.1). Its oxidation results in a rapid and significant energy release causing a pressure rise through reaction product (H_2O) gas generation and expansion, and H_2 gas evolution from heat-generated B_2H_6 decomposition. In contact with moisture, B_2H_6 is rapidly and completely hydrolyzed with copious generation of H_2 gas:

$$B_2H_6 + 6\ H_2O \longrightarrow 2\ B(OH)_3 + 6\ H_2$$

Although studied extensively by many investigators (see Section 2.3.2), the decomposition of B_2H_6 is not as well-defined with respect to various potentially influencing considerations. For the most part, B_2H_6 decomposition and, consequently, storage stability have been described in terms of pressure rise, decomposition rate, and/or composition change as a function of temperature only. Other considerations, such as the surface interaction (heterogeneous) influence, impurity types and concentrations, and pressure effects have been largely ignored.

A summary of available data and information pertinent to the storability of B_2H_6 is presented in the following paragraphs as the results from decomposition studies and storage tests.

4.1.1 Decomposition Studies

The decomposition of B_2H_6 has been studied by a large number of investigators as discussed in Section 2.3.2. For the most part, these studies were conducted to define the kinetics and mechanisms of B_2H_6 pyrolysis in conjunction with the production of the higher boranes. All of the studies involved the low-pressure (atmospheric or less) gas phase decomposition at temperatures of ≥ 50 C (≥ 122 F); none of the work characterized the facile decomposition of the liquid phase. In addition, although it was recognized in several of the studies that both homogeneous and heterogeneous reactions occur in the pyrolysis process, the catalytic activity of the containers (and the pyrolysis products) were not extensively investigated and defined. It appears that some surfaces catalyze the decomposition of B_2H_6 while others catalyze the formation of the higher boranes (i.e., they have little effect on the initial decomposition processes, but catalyze secondary reactions).

While most of the previous investigators have disagreed on the mechanism of B_2H_6 decomposition (see Section 2.3.2), most of them generally agree that the initial pyrolysis of B_2H_6 occurs by a 3/2 order reaction. In the extensive efforts reported in Ref. 4.3, which are typical of those from definitive B_2H_6 pyrolysis studies, B_2H_6 decomposition has been characterized as a function of time and temperature in a vessel (material type not reported) of fixed volume over a temperature range of 50 to 120 C (122 F to 248 F). The original data from this work, presented as a composition change with respect to time at four temperature levels, 50 C (122 F), 75 C (167 F), 100 C (212 F), and 120 C (248 F), were interpreted as percent B_2H_6 decomposition in Ref. 4.4. Illustrations of these interpreted data and an extrapolation to temperature levels of 150, 125, 100, and 77 F, are presented in Fig. 4.1 and 4.2, respectively.

The extrapolation presented in Fig. 4.2 indicates that the decomposition of B_2H_6 (gas) at 77 F (25 C) can be expressed as follows:

$$\log D = -1.44 + 0.875 \log t$$

where

D is mole percent (m/o) B_2H_6 decomposed

t is time in hours

Using this equation, ~40 m/o of the B_2H_6 would be decomposed after 120 days. This corresponds to the results from B_2H_6 storage tests at 25 C (see Section 4.1.2). This correlation also indicates 100-percent decomposition of B_2H_6 after 356 days at 25 C.

4.1.2 Storage Tests

A limited number of investigations have been conducted to determine the actual storability of liquid and gaseous B_2H_6 at various temperatures. These tests, which have been reported in Ref. 4.5 through 4.9, are briefly described in the following paragraphs and summarized in Table 4.1.

Controlled storage of liquid B_2H_6 in the mild-steel shipping containers (ullage was not specified) has been conducted by Callery Chemical Company (Ref. 4.5) at temperatures of -33, -17.8, 7 and 16 C (-27.4, 0, 44.6, and 60.8 F, respectively). These tests, which were conducted over a period of 100 days, resulted in calculation (from chemical analysis results) of the following pressure rises:

	Temperature Level			
	-33 C (-27.4 F)	-17.8 C (0 F)	7 C (44.6 F)	16 C (60.8 F)
Pressure Rise	0.15 mm Hg (0.003 psi)	0.14 atm (2.06 psi)	~1 atm (~15 psi)	~6 atm (~90 psi)

The pressure rise of ~6 atmospheres (~90 psi) at 16 C (60.8 F) corresponded to <10 percent decomposition of the B_2H_6 (Ref. 4.5). A similar storage of gaseous B_2H_6 at 25 C (77 F) over a period of 4 months resulted in a pressure rise of 52 atmospheres (764 psi); chemical analyses indicated that 40 to 60 percent of the B_2H_6 remained after the test period (Ref. 4.5).

In another series of tests reported in Ref. 4.6, no pressure rise was observed during a 197-day storage test of liquid B_2H_6 (10.5 ml) in a 43-ml stainless-steel (type unspecified) cylinder at 0 C (32 F). A 3-month storage of 12.8 ml of B_2H_6 as a gas in a 115-ml stainless-steel (type unspecified) cylinder at 0 C (32 F) resulted in an 11-psi pressure increase (from 319 to 330 psia); however, the validity of these results were questioned because of exposure of the pressure measurement system to ambient temperatures. A pressure rise of 480 psi in a third test, which involved a 4-month storage of 6.7 ml of gaseous B_2H_6 in a 43-ml stainless-steel (type unspecified) cylinder at 25 C (77 F), is graphically illustrated in Fig. 4.3; chemical analyses of the cylinder contents at the end of the test period showed 0.083 moles of H_2, 0.5 g of $B_{10}H_{14}$, and 50 to 60 percent of the original B_2H_6 content.

In studies reported in Ref. 4.7, a 100-g sample of "pure" B_2H_6 was stored in a 500-ml stainless-steel (type unspecified) cylinder at a nominal temperature of -20 C (-4 F) for a period of 13.5 months. The pressure-temperature data obtained during this period (shown in Table 4.2) indicated a pressure rise of ~16 psi; this was calculated (Ref. 4.7) as the equivalent pressure (under the test conditions) from a 0.14 percent decomposition of B_2H_6 using the mechanism of:

$$5\ B_2H_6 \longrightarrow 2\ B_5H_9 + 6\ H_2$$

Following the test, 108 cc of noncondensible gas (H_2) were measured at 25 C and 740 mm; experimental vapor pressures of five different fractions of the remaining liquid were within 4 mm of the vapor pressure for "pure" B_2H_6. It was concluded (Ref. 4.7) from this test that "diborane can be stored for long periods at -20 C without appreciable decomposition."

Short-term storage tests of liquid (and the vapor phase) B_2H_6 in contact with various metals have been reported in Ref. 4.8. In these tests, 1.2-cc samples of liquid B_2H_6 were stored in contact with 6061-T6 Al, 347 SS, and 6Al-4V-titanium specimens (1.75 by 0.25 by 0.025 inch) contained in 6-ml (0.339-inch ID by 4-inch length) cylinders fabricated from the respective metals. After 45-day storage at -78 C (-108 F), the liquid and vapor phases were removed from the cylinder and chemically analyzed by mass spectroscopy. The results of these analyses are shown in Table 4.3. Results from a similar storage (Ref. 4.8) of B_2H_6 in contact with 2 cc of <325 mesh stainless-steel oxides (prepared by burning 304 SS shim stock in gaseous oxygen), contained in a 347 SS cylinder for a period of 30 days at -78 C (-108 F) and -20 C (-4 F), are given in Table 4.3a. It was concluded (Ref. 4.8) from these studies that very little B_2H_6 pyrolysis took place as evidenced by the absence of higher hydrides, and the small amount of hydrogen produced could have been from the reaction of B_2H_6 with metal oxides, hydroxides, or hydrolysis of traces of water.

An experimental study of the effects of (simulated) in-space radiation on the storability of B_2H_6 was reported in Ref. 4.9. Stainless-steel (type unspecified) storage apparatuses with a gross volume of 14-ml were loaded with liquid B_2H_6 at 80-, 47-, and 20-percent ullages. All samples were irradiated at -108 F (-78 C) to a dose level of 10^9 erg/g (C), which was estimated to be equivalent to a 2-year exposure to the Van Allen belt radiation conditions. Following the exposures, the gas and liquid phases of each sample were analyzed by gas chromatography; the results are summarized in Table 4.4. In these tests, the only impurity found in the gas phase of the B_2H_6 samples was a small amount of H_2 which increased the overall pressure by approximately 20 psi. The liquid phase of the irradiated samples at 47-percent ullage did not contain any B_4H_{10} or B_5H_9; however, the liquid phase of the irradiated samples at 80-percent ullage contained a small quantity of B_4H_{10} (0.1 m/o), which could be formed during the irradiation by removal of H_2 from the B_2H_6, and recombination of fragments. From these results, the radiolysis damage to the samples was considered insignificant with respect to depletion of overall fuel content and there was no apparent formation of solid residue from irradiation. The production of H_2 appeared to be a gas-phase reaction of B_2H_6 because it was not affected by the liquid volume, and did not increase with increasing gas volume (11 μmole/g at 47-percent ullage; 19 μmole/g at 80-percent ullage). The failure to detect B_4H_{10} or B_5H_9, which are by-products of the H_2 reaction, was not completely understood: either their concentrations were below detection levels, or higher nonvolatile boron hydrides were formed which were not visible in an ultraviolet inspection of the irradiated product. The quantity of H_2 produced is equivalent to the decomposition of only 0.01 m/o of B_2H_6. The conclusions are that B_2H_6 suffered minor degradation with some gas evolution; however, B_2H_6 would be satisfactory for use in missions which do not involve extended durations in the Van Allen belt.

In addition to these B_2H_6 storability tests, a series of programs have been and are being performed to investigate the clogging behavior ("flow decay") of B_2H_6 during flow. These efforts which are described in Ref. 4.8 and 4.10, are designed to determine if there are soluble impurities (e.g., corrosion, decomposition, and/or reaction products) formed during B_2H_6 storage and handling that may come out of solution under flow conditions. Thus far, these laboratory studies have shown no evidence of B_2H_6 "flow decay"; however, some potential routes for this phenomena have been observed (Ref. 4.8). There have been reports (Ref. 4.11) of B_2H_6 "flow decay" during B_2H_6 engineering application studies, although no evidence of the mechanism was observed.

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4.2 MATERIALS OF CONSTRUCTION

Initial selection of materials for application in B_2H_6 storage and handling systems should be based on a series of materials compatibility tests. These tests may range from an evaluation of a material sample under a set of general test conditions to the definition of the specific limitations of various pieces of hardware fabricated from a number of different materials. Although the concern in the compatibility of materials with most propellant is usually based primarily on the ability of the material to withstand chemical attack by the propellant (as expressed by corrosion rate), the emphasis in the evaluation of materials compatibility with B_2H_6 should be placed equally on the effect of the material on B_2H_6 stability (as expressed by decomposition rate). Because B_2H_6 decomposition is probably a function of several variables, including material type, surface area, surface condition, contamination, temperature, etc., it is essential that the selection of material represent an evaluation of all of these potential effects.

The available technology on materials compatibility testing with B_2H_6 is summarized in this section. A brief description of the limited compatibility studies that have been conducted and the criteria established by these results are used to provide a basis for the selection of materials of construction for B_2H_6 service. The final evaluation of a material and its suitability for an application involving contact with B_2H_6 is based on experience resulting from that application.

In general, the recommendations of materials classification for B_2H_6 service contained herein are based on both the results of limited laboratory tests and on practical experience. In a few instances, practical experience has revealed results different from those of laboratory tests. Whenever this is the case, the greater consideration has been given to practical experience and conclusions are drawn accordingly. Criteria established for laboratory tests are based as far as possible on correlations with experience resulting from placing the materials in service.

> NOTE: The user of this handbook should be cautioned that the materials compatibility data presented herein should only serve as a basis for selection of materials for B_2H_6 service. Careful consideration should be given to the conditions of testing; the use of the material under a different set of conditions may have an entirely different effect. Materials which are not suitable for use at high temperatures may be acceptable for uses at lower temperatures. Different fabrication procedures and passivation techniques may result in variation in compatibility classification. Even different lots of the same parts fabricated from "compatible" materials by the same manufacturer using the same manufacturing techniques could result in variations in compatibility. Thus, it must be emphasized that any material used in B_2H_6 service be thoroughly tested and qualified under the conditions of its intended use before it is placed in service.

4.2.1 Compatibility Studies

There have been very few reported detailed laboratory studies of materials compatibility with B_2H_6. Whether this is an indication of the limit of the experimental characterization, or the lack of detailed documentation, can only be surmised. There are additional data available on materials compatibility resulting from the successful use of various materials in B_2H_6 production plants and operating systems; however, the basis for the original selection of most of these materials is not reported. As a result, the confidence in the use of the recommended materials over any range of conditions is somewhat questionable.

The laboratory studies of B_2H_6 materials compatibilities that have been reported are contained in Ref. 4.6, 4.8, 4.9, and 4.12. In addition to the data obtained from these studies, quantitative and semiquantitative data on materials compatibility are available from the storability studies reported in Section 4.1.2 (see Table 4.1) and can be interpreted from the chemical property data listed in Section 2.3.

The first reported (Ref. 4.6) materials compatibility studies on B_2H_6 are summarized in Table 4.5. These studies involved the contact of gaseous B_2H_6 at "room temperature" and atmospheric pressure with the listed materials contained in a glass flask. These investigators also indicated that the following materials, used in a liquid B_2H_6 handling system, were unaffected by B_2H_6.

Low carbon steel
Stainless steel
Asbestos-graphite-copper valve packing
Silicone stop-cock grease plus graphite
Vaseline-paraffin-graphite
Glyptal

They found that rusty iron causes decomposition of B_2H_6 and at atmospheric pressure, Nujol and heptane would dissolve 0.0072 and 0.26 g B_2H_6/100 ml, respectively. As a result of the studies, it was concluded (Ref. 4.6) that B_2H_6 appears to be safe with all the common metals, but the oxides of many metals are not inert to it. They indicated that B_2H_6 can be expected to be compatible with those organic substances which have no functional groups and are completely saturated; however, it tends to dissolve in organic fluids, particularly under pressure.

In studies reported in Ref. 4.9 (see Section 4.1.2), two seal compositions, nylon and Kel-F (plastic) were irradiated [10^9 erg/g (C)] as installed in test fixtures in the presence of liquid B_2H_6 (-108 F). Although both test fixtures suffered an apparent fuel loss of 6.4 percent, this effect was apparently caused by an unobserved error occurring during the filling operation. From the results of these tests summarized in Table 4.6, it was concluded that both seals were satisfactory for use under the indicated conditions. "The initial compression set acquired by both plastics proved to be essentially permanent. Neither type changed significantly in weight, although the nylon O-rings typically turned from white to a straw yellow color. The hardness of both type O-rings remained unchanged during test, while the tensile strength increased in each case--almost 20 percent in the case of the nylon seals. Resiliency was lower in the irradiated Kel-F O-rings than in the controls, while the nylon O-rings underwent no detectable change in resiliency." (Ref. 4.9)

During work (Ref. 4.12) performed to identify and characterize elastomers suitable for use as expulsion bladders for B_2H_6 (and OF_2), propellant compatibility and permeability tests were used to screen commercially available, cured, unfilled elastomers and evaluate selected elastomers with fillers. Three polymers, peroxide-cured Nordel 1145 EPT (DuPont), zinc oxide- and peroxide-cured HYCAR 1072 Nitrile (Goodrich Chemical Company), and peroxide-cured W-970 Silicon (Union Carbide) were screened in B_2H_6 at -78.5 C (-109 F) and 0 C (32 F); the Nordel 1145 candidate was degraded during the test and, consequently, eliminated from further considerations. Further evaluation of the HYCAR 1072 and W-970 polymers and a CIS-4 1203 polybutadiene (Phillips Petroleum Company) polymer, all cured and reinforced with SiO_2, indicated that the HYCAR 1072 butadiene/acrylenitrile polymer appears to be compatible with gaseous and liquid B_2H_6. In addition, helium and B_2H_6 gas permeability tests were run with this elastomer. "At 0 C (32 F) or even at -20 C (-4 F), this polymer is extremely flexible and could probably be used for bladder construction; at -78.5 C (-109 F) the polymer is stiff. Gas permeability at -20 C (-4 F) is low, in the range of air through a toy natural rubber balloon. A tradeoff between low temperature stiffness and chemical compatibility may be obtained by varying the monomer ratio of the nitrile polymer." (Ref. 4.12) The results of these studies, which are summarized in Table 4.7, have provided guidelines for additional studies in progress under Contract NAS7-770.

The results of 45-day corrosion testing of 347 stainless steel, 6Al-4V-titanium, and 6061-T6 aluminum in the liquid and vapor phases of B_2H_6 at -78 C (-108 F) have been reported in Ref. 4.8 and are summarized in Table 4.8. From these tests, it was concluded (Ref. 4.8) that the aluminum alloy was most affected (although to a minor degree), while titanium was minimally attacked and stainless steel the least affected. In other tests involving stainless-steel oxides (formed by the combustion of 304 SS shim stock in gaseous oxygen) stored in B_2H_6 for 30 days at -78 C (-108 F) and -20 C (-4 F), some of the metal oxides were reduced to the metal, indicating a potential problem area ("cold-welding") with rubbing or sliding surfaces unless the metal surfaces are deoxidized (freshly polished) prior to use in B_2H_6. Results of chemical analyses of the B_2H_6 from these corrosion tests have been summarized in Tables 4.1 and 4.3. These investigators also reported (as a result of a private communication of other work, Ref. 4.13) that there have been surface cracks observed in the storage of boron hydrides in maraging steels.

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4.2.2 Materials Selection for B_2H_6

Based on results of the compatibility studies described in Section 4.2.1 and the operating experience reported by several investigators (Ref. 4.1, 4.2, 4.6, and 4.14), various materials have been rated for service in B_2H_6. Such ratings have been previously presented in Ref. 4.1, 4.2, and 4.14 through 4.19. In general, these ratings indicate that most of the common metals are satisfactory for use with B_2H_6; however, the oxides of these metals and other surface contaminants may be reduced by B_2H_6 (or cause B_2H_6 decomposition) and precautions should be taken to prevent their formation. Most rubbers and some other nonmetallic materials are attacked by B_2H_6; thus, some care must be exercised in the selection of seals, gaskets, lubricants, solvents, etc.

A summary of the presently accepted ratings is presented in the following paragraphs as a guideline for the selection of materials for B_2H_6 service. It is strongly emphasized that these ratings are based primarily on gross qualitative results and more definitive testing might be required in critical areas. Also, it is pointed out that these ratings do not differentiate between the liquid and gas phases nor indicate temperature limitations; thus, the physical limitations relative to these factors must also be considered in materials selection.

4.2.2.1 Compatible Materials. The following materials have been recommended as compatible for use with B_2H_6:

Metals and Metal Alloys

aluminum*
low carbon steel*

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*See NOTE at end of Section 4.2.2.2

4.2.2.1 Compatible Materials (Continued)

chrome-moly-steel

stainless steel 18-8

stainless steel series 300

6Al-4V-titanium

brass

copper*

lead

Monel

K-Monel

nickel

soft solder

Nonmetals

Saran

Viton A, Fluorel, or equivalent asbestos graphite (Garlock or equivalent)*

tetrafluoroethylene (TFE, Halon TFE, Teflon, or equivalent)

polychlorotrifluoroethylene (Kel-F, Halon CTF, or equivalent)

50-50 polyethylene-polyisobutylene

polyethylene

Mylar

Hycar rubber*

HYCAR 1072 butadiene/acrylonitrile elastomer, unfilled and SiO_2-filled*

pure dry asbestos or tetrafluoroethylene-impregnated asbestos

JM-76

Nylon

Glyptal

Crane lead seal

Shellac-graphite paste

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*See NOTE at end of Section 4.2.2.2

4.2.2.1 Compatible Materials (Continued)

Lubricants

- perfluorocarbon lubricants
- Fluorolube FS
- vaseline
- paraffin
- graphite
- high vacuum silicone grease
- DC 33 silicone grease
- "T-film" (Eco Engineering)

Solvents

- alcohol
- kerosene
- JP-4
- JP-5
- pentane
- Nujol

4.2.2.2 Prohibited Materials.

The use of the following materials with B_2H_6 is not recommended:

- metal oxides
- maraging steel*
- magnesium*
- natural rubbers
- neoprene
- many other synthetic rubbers*
- Leak-lock
- Permatex
- ordinary oil and grease
- Nordel 1145 EPT elastomer, unfilled and SiO_2-filled

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*See NOTE at end of Section 4.2.2.2

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4.2.2.2 Prohibited Materials (Continued)

W-970 silicon elastomer, unfilled and and SiO_2-filled

ClS-4 polybutadiene elastomer, unfilled and SiO_2-filled

(See Section 4.2.3.2 for potentially shock-sensitive solvents)

*NOTE: Some disagreement or question exists with these materials: aluminum is reported as incompatible in summary of Ref. 4.20 while work of Ref. 4.8 indicates insignificant attack on 6061-T6-Al; maraging steel is reported as incompatible with boron hydrides in Ref. 4.8; mild steel and copper are reported as incompatible in Ref. 4.19, while all other references indicate compatibility with B_2H_6; magnesium is reported as incompatible in Ref. 4.20, although most references indicate that compatibility has not been tested; and all rubbers are reported incompatible in Ref. 4.15, while Hycar rubber, HYCAR 1072, and Viton A, etc., are reported compatible in Ref. 4.14, 4.12, and 4.2, 4.14, and 4.15, respectively.

4.2.3 Materials Selection for Related Boranes

More extensive efforts have been conducted in materials compatibility testing with other boranes (principally B_5H_9). Although the temperature application ranges of these other boranes are significantly different than that of B_2H_6 and they are not so susceptible to decomposition within the earth-storable temperature range, the data on these other boranes might provide an additional guide in the preliminary planning and selection of materials for a B_2H_6 system. However, they must be tested prior to actual use. The materials ratings for pentaborane, contained in the following paragraphs, were taken from Ref. 4.15 and 4.21.

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4.2.3.1 Compatible Materials. The following materials have been recommended as compatible for use with PENTABORANE:

Metals and Metal Alloys

- 5052-S Al
- 6061-T6 Al
- 7075-T6 Al
- Cadmium coated Al
- Chromated Al
- 2024-T3 Al
- 3003-H14 Al
- 356-T6 Al
- Anodized Al
- 18-8 stainless steel
- low carbon steel
- K-monel
- Monel M-8330-B
- nickel
- Nichrome "V"
- magnesium Fed-QQ-M-44A
- magnesium Fed-QQ-M-56-A263
- titanium C-130AM and C-110AM
- copper
- brass
- Hastelloy
- cadmium cadmium plating

Nonmetals

- polychlorotrifluoroethylene (Kel-F, Halon CTF, or equivalent)
- fluorosilicone rubbers
- tetrafluoroethylene (TFE, Halon TFE, Teflon or equivalent)
- glass
- dry asbestos

4.2.3.1 Compatible Materials--PENTABORANE (Continued)

carbon
Fluoroflex T or equivalent
Viton A and B or equivalent
Garlock 230 or equivalent
Pyrex
Barlack 230
Velumoid
graphite impregnated asbestos
polyethylene
polypropylene

Lubricants

perfluorocarbon lubricants
Graphitar No. 39
Rockwell Nordstrom Lube No. 921
Gulf Harmony Oil No. 44 and 69
Hercules No. 571 Kaobestos
vaseline
paraffin

4.2.3.2 Prohibited Materials. The following materials have been found to be unsatisfactory for use with PENTABORANE:

natural rubber
water-based lubricants
vinylidine plastics
epoxy cements
Foamglass (with binder)
graphite and carbon (with binders)
Rockwell-Nordstrom Lubes No. 833, P-21, 860, 386, 852-S, P-55, and 942-S
butyl rubbers
nylon
Mylar
Tygon

Saran
GR-S rubbers
neoprene
buna rubber
silicones
polyurethane
Johns Manville 2086 and G-255

In addition, the following is a list of solvents, which will form shock-sensitive mixtures with PENTABORANE:

chloroform
dioxane
acetone
aldehydes
ketones
carbon tetrachloride
trichloroethane
special fluorinated solvents
trichlorethylene
halogenated compounds

4.3 MATERIALS TREATMENT AND PASSIVATION

4.3.1 General Philosophy of Passivation

All materials that come in contact with B_2H_6 must be thoroughly cleaned and chemically treated prior to their use to minimize B_2H_6 degradation and possible materials corrosion. The general terminology applied to this process, which is designed to provide an inactive surface and eliminate potential contamination sites, is passivation. In general, the philosophy that has been employed in the passivation of B_2H_6 components, equipment, and systems is very similar to that used to clean most propellant systems and is essentially directed at the achievement and maintenance of "LOX cleanliness" criteria.

The passivation procedure for most propellants essentially consists of three steps prior to the material's contact with the propellant. The initial step is a chemical and physical ("cleaning") procedure designed to remove oxides, scale, dirt, weld (and heat treat) slag, oil, grease, and other foreign material from the base material. The second step is usually the treatment ("basic passivation") of the material with an alkaline or acid solution to establish a "fresh" surface of the material and eliminate foreign material particles established during machining, welding, heating, etc. Finally, the material is subject to conditioning ("propellant passivation") with a diluted form (either as a gas or a diluted liquid phase) of the propellant to check the completeness of the chemical treatment, and possibly, eliminate any remaining active sites through diluted reactions. In passivation of B_2H_6 components and systems, this procedure is uniformly followed through the "basic passivation" step; the usefulness or protection of the "propellant passivation" step has not been investigated or established, and its employment is arbitrary.

In performance of the passivation, the material surfaces should be subjected to passivation after part fabrication and before component or system assembly. Basically, items such as valves, actuators, system piping, etc., cannot be cleaned in the assembled state because the solvents or cleaning solution may damage nonmetallic parts, or may be trapped with residues in inaccessible areas. Therefore, cleaning should be done immediately before component or system assembly, unless provisions are made for packaging the passivated part to protect against recontamination until ready for assembly. After assembly, components, such as valves, should be packaged until they are utilized in the final system assembly.

All cleaning, passivating, and rinse solutions should be applied by immersing, spraying, wiping, circulating, or other manner so that all surfaces to be cleaned will be completely wetted and flushed with the solutions. Any section of the item to be cleaned that can trap or retain any liquid should be drained or emptied between the applications of each different solution of chemical mixture. The item should be rinsed until it is chemically neutral between each operation. Surfaces should not be allowed to dry off between cleaning and "basic passivation" steps. The water used should be distilled, deionized, or clean, potable tap water (for preliminary washing and rinsing), filtered through a 40-micron nominal filter. Unless otherwise specified, all chemicals should be C.P. (chemically pure) grade or better.

The development and use of special material, component, and system passivation procedures specifically for B_2H_6 service has been limited. Most of the procedures have evolved from LOX cleaning techniques or those used for pentaborane service. Some of the techniques previously or primarily used in passivation for B_2H_6 service are described in Ref. 4.21 through 4.24. The following procedures are recommended (Ref. 4.15) for all boranes by the JANNAF Hazards Working Group of the JANNAF Propulsion Committee, because they offer insight into the general level and thoroughness of cleaning required. However, many special problems and circumstances may be encountered when systems are prepared for B_2H_6 service, and specific procedures should be developed (following the general philosophy and approach described in the recommended procedure) as needed.

NOTE

The fumes of acids, alcohols, and degreasing solvents used in this procedure are toxic and work areas should be well ventilated. Vats of nitric acid solution used for pickling should be covered and externally vented. Iron accidentally placed in nitric acid produces nitrogen dioxide (NO_2) fumes which are highly toxic.

4.3.2 Metal Components

4.3.2.1 Disassembly. Equipment must be thoroughly decontaminated before disassembly if it has been in prior service. Valves, fittings, tubing, regulators, etc., are first disassembled into their component parts, except for plastic inserts that may be damaged by removal.

4.3.2.2 Solvent Degreasing. Exceedingly greasy or dirty parts are wiped free of loose dirt and grease and cleaned with solvent degreaser or vapor. A halocarbon solvent such as trichlorotrifluoroethane (Freon TF or equivalent commercial grade) is recommended. The following degreasing solvents may also be used:

perchloroethylene (inhibited tetrachloroethylene, ethylenetetrachloride-commercial grade)
trichloroethylene (inhibited ethinyl trichloride-commercial grade)
methylene chloride (dichloromethane-commercial grade)
methyl chloroform (1,1,1-trichloroethane-commercial grade)

The parts are degreased with solvent or solvent vapor for 30 minutes. Plastic parts or parts containing plastic inserts which may be softened by the solvent should be cleaned separately (see Section 4.3.3).

Degreased parts are rinsed well with Type IIIA ethyl (MIL-A-6091C) or isopropyl (commercial grade) alcohol and then with distilled, particle-free dionized, or clean potable tap water.

> NOTE
>
> The halogenated solvents must be completely removed. If any residual solvent is trapped, it will react explosively with boranes.

Handle all parts with clean gloves after degreasing.

4.3.2.3 Detergent Cleaning. Brass, nickel, Monel, copper, lead, and stainless-steel parts are placed in a 4-percent detergent solution (6 ounces of Dreft, Tide, or similar products to 1 gallon of water) for 30 minutes with the temperature controlled at 120 F (49 C). The temperature may be raised if no plastic parts are present, but it should never be over 150 F (65.5 C). Rinse the parts several times with water (distilled or particle free deionized water). Aluminum parts are cleaned in a similar manner with a 4-percent solution of aluminum cleaner (6 ounces of Turco Product 3266 or equivalent to 1 gallon of water) for 30 minutes and then rinsed thoroughly with distilled or particle-free deionized water.

4.3.2.4 Acid Pickling. Place stainless-steel parts in a bath of 40- to 50-percent nitric acid (7 parts commercial-grade 70 percent nitric acid with 3 parts water; 5 parts 100-percent nitric acid with 5 parts water; or 4 parts IRFNA with 6 parts of water) for at least 1 hour. (Omit this step for other metals, alloys, or fully machine-finished stainless-steel parts.) Castings and rough-finished parts should remain in the nitric acid for a longer time. Rinse with distilled or particle-free deionized water.

4.3.2.5 Special Step. Place the parts in commercial-grade isopropyl or MIL-A-6091C, Type IIIA ethyl alcohol for 15 minutes, then proceed to the final treatment.

4.3.2.6 Final Treatment. For all metal parts used with the boranes, continue with the following steps:

a. Steam parts clean.

b. Blow parts absolutely dry with nitrogen gas (free of oil and moisture).

c. Package each small part in a polyethylene bag (ACLAIR 33C or equivalent) and close the bag securely until the part is to be used. Cover the opening and the clean areas of each large part with polyethylene film and tape until part is to be used.

4.3.3 Plastic Components

All O-rings, gaskets, and other nonmetallic plastic components are cleaned as follows:

a. Clean parts with a 4-percent detergent solution (6 ounces of Dreft, Tide, or similar product in 1 gallon of water) for 30 minutes at 120 F (49 C).

b. Rinse parts with distilled water several times.

c. Blow parts dry with oil- and moisture-free nitrogen gas.

d. Package parts in polyethylene (ACLAR 33C or equivalent) bags until they are to be used.

4.3.4 Stainless-Steel Tanks

4.3.4.1 Preparation.

a. Inspect tank for rust, dirt, scale, etc.

b. Remove rust and scale mechanically.

4.3.4.2 Cleaning.

a. Degrease tank with solvent (see Section 4.3.2.2) at 150 F (66 C)

b. Rinse tank thoroughly with commercial-grade isopropyl or MIL-A-6091C, Type IIIA ethyl alcohol.

c. Rinse tank thoroughly with distilled, particle-free dionized, or clean potable tap water, or steam clean.

d. Fill tank partially with 4-percent detergent solution (see Section 4.3.2.3) and heat to 150 F (66 C) for 30 minutes. Rinse with clean water.

4.3.4.3 Welds.

a. Inspect inside of tank, especially welds. If tank and welds are visibly clean and bright, proceed directly to procedure Section 4.3.4.4. If welds are blackened, add enough nitric acid/hydrofluoric acid mixture (5 parts 50-percent reagent grade HF acid with 95 parts of 50-percent nitric acid) to cover welds for 30 minutes and rinse with distilled, particle-free deionized, or clean potable water.

b. Inspect welds again. If still black, repeat step (a). If the welds are no longer black, rinse tank thoroughly with distilled, particle-free deionized, or clean potable tap water, or steam it clean.

4.3.4.4 Special Step. Wash inside of tank thoroughly with commercial-grade isopropyl or MIL-A-6091C, Type IIIA ethyl alcohol for at least 15 minutes; fill tank if possible, then proceed to final treatment.

4.3.4.5 Final Treatment.

a. Fill tank completely, and wash thoroughly with distilled or particle-free deionized water.

b. Blow tank dry with oil- and moisture-free nitrogen and cover all openings with polyethylene film.

4.3.5 Aluminum and Aluminum-Alloy Tanks

Although aluminum is not in current use with B_2H_6 because of the lack of materials compatibility data, the following procedure is that employed for its use with other boranes.

4.3.5.1 General.

a. Inspect inside of tank and remove burrs, grease, dirt, scale, etc.

b. Degrease tank with vapor or liquid solvent (see Section 4.3.2.2) for 30 minutes.

c. Rinse the tank with commercial-grade isopropyl or MIL-A-6091C, Type IIIA ethyl alcohol.

d. Wash it thoroughly with distilled, particle-free deionized, or clean potable tap water.

e. Add 4-percent aluminum cleaning solution (see Section 4.3.2.3) for 20 minutes at room temperature. Revolve tank so that solution covers the entire tank, or scrub walls.

f. Wash tank thoroughly with distilled, particle-free deionized, or clean potable tap water, or steam it clean.

g. Inspect tank; it should be bright and clean.

4.3.5.2 Special Step. Fill tank with commercial-grade isopropyl or MIL-A-6091C, Type IIIA ethyl alcohol solution for 15 minutes, or scrub tank walls thoroughly. Then proceed with final treatment.

4.3.5.3 Final Treatment.

a. Wash tank thoroughly with deionized or particle-free distilled water, or steam it clean.

b. Blow it dry with oil- and moisture-free nitrogen and cover all openings with polyethylene film.

4.3.6 System Assembly

4.3.6.1 General. In assembling the system (also see Section 4.4.3), only clean, degreased tools should be used. The assembler shall wear clean, lint-free gloves and outer garments. Small components shall be assembled in a clean, dust-free room. Insofar as possible, keep all openings and clean surfaces covered with polyethylene film until the system has been assembled.

4.3.6.2 Final Preparation.

a. All assembled systems shall be kept clean by closing all openings or covering them with polyethylene film and by maintaining a clean, dry nitrogen atmosphere inside.

b. Diborane systems must be purged with dry nitrogen gas to ensure that the system is absolutely free of air (oxygen) and moisture.

c. Check every system for leaks at operating pressure with clean dry helium gas.

4.4 FACILITIES AND EQUIPMENT

4.4.1 Facility Design Considerations

A facility for the storage and handling of B_2H_6 may exist in the form of: (1) a singular storage facility for B_2H_6 only, (2) a

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special handling area for B_2H_6 such as a laboratory area, (3) a storage complex for fuels including B_2H_6, (4) an area storage complex for fuels and oxidizers, or (5) a handling complex for various propellants. Although it is desirable that any such facility be located in an isolated area, if necessary, it may be located in the proximity of a test or launch facility.

The specific design criteria for each type of B_2H_6-containing facility must be considered independently, although most considerations apply to all facilities. This is necessary because any other propellants stored or handled at the facility also require special considerations. In addition, a facility located in the proximity of a launch or test installation, for example, is exposed to vibrational, thermal, and possibly shrapnel effects, all of which require special considerations.

The design principles presented in this handbook apply to those criteria associated with storage and handling facilities for B_2H_6 only. Thus, in the use of these criteria in areas where other propellants are stored and/or handled, the facility designer must consider the integration of various other requirements in his design of the B_2H_6 facility.

4.4.1.1 Facility Layout and Orientation. Diborane storage and handling areas should be situated in such a manner as to provide the least hazard to surrounding facilities and personnel under any given condition. Because the layout of test areas is dependent upon particular requirements and considerations in which many attendant hazards must be accepted, the layout considered here is related primarily to storage or handling areas which can be situated as desired.

In addition to provisions for the required equipment and facilities as well as for possible expansion, the arrangement and layout of B_2H_6 storage and handling areas should be in accordance with criteria established in Ref. 4.25 through 4.29 (as summarized in Ref. 4.15). The areas should be oriented so that the prevailing winds do not carry vent gas, vapor from leaks and spills, or vapor from disposal and treatment areas into work and service areas, parking areas, or roads carrying heavy traffic. As such, the following criteria should be considered.

4.4.1.1.1 Meteorological Considerations. All atmospheric dispersal equations indicate that the ground level concentration of gases or smokes in air is inversely proportional to the square of the height of release above an aerodynamically smooth plain if release is continuous, and inversely proportional to the cube of the height of release, if release is instantaneous (Ref. 4.30). Thus, B_2H_6 storage and gross handling areas should be located at the highest accessible elevations in such orientation that the prevailing wind in that area will carry vapors from spillage toward unpopulated areas or over the top of a ridge which elevates the effective height of release. A detailed discussion of meteorological considerations in the handling of B_2H_6 (and OF_2) at Kennedy Space Center and the Air Force Eastern Test Range at Cape Kennedy is presented in Ref. 4.31.

4.4.1.1.2 Quantity-Distance. Because of its low boiling point, B_2H_6 undergoes a rapid vaporization at ambient temperatures and presents an ever-present toxic hazard to downwind areas during storage and transfer. Criteria for the specific location of B_2H_6 storage and handling sites in relation to surrounding habitation and public transportation are summarized in Ref. 4.15 (from criteria given in Ref. 4.25 through 4.29). The quantity-distance table (Table 4.9) was extracted from this reference. This table presents the limiting values for Storage Compatibility Group D substances of the Hazard Group III propellant classification (which includes B_2H_6). The definitions for these groups are as follows:

COMPATIBLE STORAGE--GROUP D

These compounds act mainly as fuels, but individual members may be oxidizers in some combinations. They may be a monopropellant with the right catalyst, or they may be pyrophoric and ignite upon release to the atmosphere. Special temperature storage requirements are necessary for some members of Group D.

HAZARD GROUP III

The hazards from these assigned materials are primarily due to possible storage container pressure rupture, resulting from an adjacent fire and from vapor phase explosions within the Group III container. Either the pressure rupture or a vapor phase explosion produces a fragment hazard from the container, its protective structure and other adjacent material.

4.4.1.2 Storage Facilities. Diborane storage can be integrated with storage facilities for other boranes and ethylene oxide (see Table 4.10). The area layout should allow for easy access and egress for loading and unloading vehicles and adequate separation of the bulk storage tanks from each other and from the cylinder storage area. All storage tanks and associated valves and piping should be located aboveground to facilitate the detection of leaks. All main tank connections should be made through the top portion of the tanks to reduce the possibilities of propellant spill.

Diborane is normally stored as a liquified compressed gas and should be kept at a temperature level <-4 F (<-20 C) to prevent decomposition. Thus, the storage facility must be equipped to refrigerate the storage containers. This may be accomplished through use of dry ice, a dry ice slush, low temperature units, jacketed containers using regulated liquid nitrogen flow, etc.

Both bulk and ready storage of these compounds can be accomplished either in the shipping cylinders or in permanent facility storage tanks. When the shipping cylinders are used for bulk storage, they can be stored in groups and each group treated, for facility design purposes, as a storage tank. Provisions should be made to unload each group of cylinders simultaneously. Chocks or steel cradles should be permanently positioned to prevent movement of cylinders.

Permanent facility storage tanks should be sized to receive several individual shipments, with a relatively large volumetric allowance for ullage. The tank supports and foundations should be designed with a minimum safety factor of 4, taking into consideration local seismic and vibrational conditions. Each tank should be electrically grounded and equipped with an adequately sized, remotely controlled, "fail-safe" vent valve. A well must be provided at the bottom of the storage tanks to permit almost complete propellant drainage. The well may, in turn, be completely drained for cleaning purposes by providing an adequate tank connection.

A schematic representation of a typical cylinder storage and unloading installation, used in B_2H_6 handling operations reported in Ref. 4.24, is presented in Fig. 4.4.

4.4.1.3 Transfer Systems. Propellant transfer systems should be arranged and connected to permit safe (see Section 6.2.1) and systematic transfer of B_2H_6 without loss or contamination. Valves and lines should be sized to provide efficient transfer without excessive pressure loss. Materials of construction and fabrication methods, coupled with passivation procedures should be adequate for extended service in B_2H_6. The transfer system should be adequately insulated, refrigerated, or vacuum jacketed to maintain B_2H_6 below or within an acceptable decomposition temperature range.

System components should be adequately and rigidly supported with consideration for temperature changes. The possibility of propellant leakage can be significantly reduced by using all-welded pipe lines with flanged end connections. System components should be located within the diked area to facilitate spillage control. The inlet and discharge terminals of transfer lines should be valved. The transfer lines should be designed and installed to provide for adequate drainage and purging.

The tank vent lines should be piped into a gas scrubber, a flare stack, or a high vent stack (see Section 4.5.5). If a vent stack is used, the effluent vapor should be released at least 60 feet from the highest working point in the area. Regardless of the vapor disposal method utilized, the vent lines should be equipped with an appropriate flame arrestor.

Diborane can be unloaded from the storage tanks and shipping cylinders by means of its own vapor pressure or gas pressure, or by pressurizing the tank with oil-, moisture-, and oxygen-free gaseous nitrogen or helium. (Helium may be preferred because of the high solubility of N_2 in B_2H_6--see Section 2.2.2.7.) Although the use of a transfer pump might be preferred, there is no acceptable pump for B_2H_6 at the present time (Ref. 4.15).

4.4.1.4 Diking and Retainment. Each B_2H_6 storage tank and/or group of shipping cylinders should be installed within a separate dike, revetment, or walled area to retain spilled propellant. The dike or retainment should be capable of retaining at least 110 percent of the tank or cylinder group's storage capacity (Ref. 4.15). The diking system should be designed so that it will gravity-drain into a burn basin, a collection basin, and a reclamation sump. These facilities can be interconnected by means of valves. Because it is likely that B_2H_6 will vaporize and ignite upon spillage, this retainment system is primary for the control and disposal of borane residues and solutions (see Section 6).

4.4.1.5 Buildings. Buildings or shelters should be provided for shade, ventilation, and weather protection of the B_2H_6 shipping cylinders from the sun. Large tanks should be painted with heat reflecting paint, if it is impractical to shade them. The buildings should be of the roofed, open-shed type, or prefabricated aluminum with overhanging eaves. The building should be well ventilated to prevent the accumulation of B_2H_6 vapors. If siding is used, a screen ventilating area of at least 1 foot should be maintained between the siding and the floor. All construction materials should be normally nonflammable and a concrete floor is recommended.

4.4.1.6 Safety and Fire Protection (Refer to Section 6). Good system design and development, observation of good operating procedures, and good housekeeping are the best safety precautions in B_2H_6 storage and handling areas. These areas must be kept neat, clean, and absolutely free of any type of combustible material. All leaks and spills should be sprayed (fog nozzle) immediately with copious amounts of water. Frequent inspection of the areas to ensure compliance with these regulations should be maintained.

Storage and handling areas shall be provided with personnel emergency showers, eye baths, fire blankets, portable fire extinguishers, first-aid kits, and a water deluge system, preferably of the fog type. Safety equipment shall be strategically located and easily accessible. All operating personnel shall be thoroughly familiar with the location and operation of each piece of safety equipment. The operation of the equipment shall be verified periodically. A reliable borane detector (see Section 6.3.1) should be used to help in monitoring storage and drainage collection points.

4.4.1.6.1 Personnel Education. Standard operating procedures should be established for all operations and potential situations that might occur in B_2H_6 storage and handling areas. Thorough education of all operating personnel with respect to these procedures is mandatory. In addition, these areas should be restricted to a minimum number of previously authorized personnel required for operation and safety.

4.4.1.6.2 Personnel Protection. Proper protective clothing and respiratory protection (see Section 6.4.1.2), an adequate number of deluge safety showers and eye baths, and easy egress from the area should be provided for the protection of operating personnel. This equipment should be clearly located and marked.

4.4.1.6.3 Facility Protection. An adequate water supply must be available for fire fighting, flushing and decontamination, equipment and facility cooling, and personnel safety equipment. The water spraying system should be fabricated of pipe not less than 1 inch in diameter and provided with a nozzle pressure of at least 50 psig. The locations for floor flushing, drainage flooding, and fire protection valves (either for hoses or fixed nozzles) should be clearly marked by signs and red lights. In addition, the propellant handling areas should be provided with portable, chemical-type and carbon dioxide fire extinguisher for general use throughout the area (see Section 6.3.3).

4.4.1.7 Electrical Concepts. All electrical installations throughout the B_2H_6 storage and handling areas should conform to the national, state, and local codes for the type of area and service involved. The electrical installation in hazardous locations in transfer and storage areas, shall conform to the requirements given in Section 500 of the National Electrical Code (Ref. 4.32), Class I, Group B, Division 1 or 2, depending upon occupancy of the area.

Electrical power distribution within the areas should be through rigid aluminum or steel conduits, which are preferably located underground. Motors, controls, switches, relays, lights, etc., should be explosion proof or as otherwise stated in this code. Adequate electrical receptacles should be strategically located for maintenance purposes, and the areas should be flood-lighted in accordance with good industrial and safety practices for the type of operation involved.

All vent stacks, storage tanks, and steel structures should have integrally mounted lightning protection systems in accordance with Section 8 of Ref. 4.33. All storage tanks, pumps, loading points, electrical equipment, and propellant transfer lines should be grounded and bonded electrically, in accordance with national, state, and local codes. Sparks from static electricity can ignite B_2H_6-air mixtures, that might not otherwise ignite.

4.4.1.8 Ventilation. Good ventilation is essential in the handling of B_2H_6 to prevent the accumulation of explosive and toxic concentrations. Confined or closed areas must be ventilated; open-side buildings are recommended where the weather permits. If natural ventilation is not adequate, all storage and transfer structures shall be equipped with approved ventilating systems, either for constant use or as a safety measure before personnel entry. Provisions should be made for emergency ventilation of 30 to 60 air changes per hour. The fans must be of spark-proof construction.

4.4.1.9 Drainage. All operational areas shall be provided with proper drainage, so that leaks and spills can be immediately flushed away with copious amounts of water. Drainage shall be so arranged as to prevent boranes from mixing with grossly incompatible materials.

4.4.1.10 Access Roads. At least two access roads to transfer and storage sites should be provided, with adequate space at each site for turning.

4.4.1.11 Fencing. Storage and handling areas, drainage ditches, and catch ponds should be fenced and equipped with warning signs, safety placards, and other equipment and techniques typical of good industrial practice.

4.4.2 Equipment Design and Selection Criteria

In the design of an item of equipment for B_2H_6 service, the same basic principles of design apply as for any other fluid-handling system. For B_2H_6 service, simplicity in design is essential. Attempts should be made in the design to minimize cracks, crevices, dead end or pocket areas, vessel openings, and the number of connections. Welded and flanged connections are preferred to threaded connections. The number of parts in a system or component assembly should be kept at a minimum that is consistent with the mechanical and structural requirements of the equipment, and the equipment must be designed so that all units can be easily disassembled into component parts for ease in passivation and inspection.

Throughout the design and layout of a B_2H_6 system, the potential integrity of the system with respect to cleanliness and compatibility with the B_2H_6 must be constantly reviewed. The use of each material and its potential contact with the propellant must be consistent with the material compatibility data, as illustrated in Section 4.2.2.

The list of reference material included is a compilation of readily available data to facilitate the design and specification of systems handling B_2H_6. Manufacturers listed herein are typical only for the type of product; the list does not restrict the field to those mentioned, or eliminate those not mentioned.

All systems should include suitable filters to filter purge, blanketing, or pressurizing gas before it enters the systems. All purge, pressurizing, and inert blanket gas should be dehumidified to a dewpoint of -65 F or lower. Because of the constant hazard of insoluble (e.g., higher boranes, B_2O_3, etc.) particles in B_2H_6 systems, all streams of propellant should be filtered during transfer from one system to another. In-system filtering should be conducted, wherever feasible.

Piping and vessel systems should be electrically bonded and grounded so that the maximum resistance from flange to flange shall not exceed 10 milliohms and the resistance from any part to the ground shall not exceed 25 milliohms.

Because B_2H_6 is pyrophoric (under practical considerations), extremely toxic, and reacts readily with moisture, etc., all equipment and systems must have a high degree of integrity and positive sealing characteristics.

Typical equipment design and selection considerations are presented in the following paragraphs. Although these considerations will aid the B_2H_6 user in the design of B_2H_6 storage and handling systems, they are not intended as a substitute for good engineering practices nor do they exclude other competent and knowledgeable considerations. It is also noted that the following criteria are primarily for semipermanent or permanent facilities and do not apply to flight hardware, although many of the considerations may be applicable.

4.4.2.1 Storage Vessels. All pressure vessels for B_2H_6 storage and feed should be designed and constructed in accordance with ASME boiler and pressure vessel code, Section VIII, latest edition

(Ref. 4.34) as a minimum. Also, all pressure vessels shall be designed and constructed to satisfy applicable local and state codes for vessels. All other vessels for B_2H_6 service should be designed and constructed in accordance with good engineering practice for the pressure and service in which they are to be used. Bottom outlets and openings should be avoided. A minimum factor of safety of four for vessel and vessel support material strength should be maintained in all designs. Due allowance shall be made for temperature conditions, internal and external corrosion, and local seismic and atmospheric disturbances. All vessels shall be of seamless welded construction.

As noted elsewhere (see Sections 4.4.1.2 and 5.1) in this handbook, the B_2H_6 shipping containers are suitable for bulk-and-ready-storage of the propellant, if they are suitably located, protected, and refrigerated. Permanent bulk and ready-storage tanks, run tanks, and missile system tanks can be fabricated from any of the compatible materials noted in Section 4.2, although the AISI 300 series stainless steels are presently preferred (because of their properties and a greater use history).

The vessels should be designed with a minimum number of openings to prevent accidental contamination. Because B_2H_6 is a liquified compressed gas that must be kept at a temperature level of <-4 F (<-20 C) to prevent decomposition (see Section 4.1), suitable provisions must be made in the design of the tank or in storage of the shipping cylinders for the refrigeration and insulation of the propellant. This may be accomplished by a number of techniques, of which the preferred method (Ref. 4.31) is the controlled flow of liquid nitrogen through a surrounding jacket or internal flow passages. A description of a proposed combination transportation and storage container (see Fig. 53) is given in Ref. 4.3.1.

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4.4.2.2 Piping Systems. Information of a general and specific nature relating to pipe, pipe material, and piping installation is extensively covered in Ref. 4.35 through 4.39.

4.4.2.2.1 System Design. All piping used in the storage, venting, and transfer of B_2H_6 should be designed in accordance with Sections 3 and 6 of Ref. 4.35. Allowable tensile stresses for pipe materials are listed in Table 12 of Ref. 4.35. Material specifications for pipe, fittings, valves, flanges, tubing, and boltings are listed in Table 8 of Ref. 4.35.

In designing a B_2H_6 system, care should be taken to provide drainage and avoid traps so that system drainage is complete. Stagnent pools and dead ends in elevated temperature areas must be avoided to prevent pressure buildup from decomposition. Where trap conditions are unavoidable, drain valves should be provided. Provisions must be made to decontaminate all B_2H_6 systems with an inert solvent. This also includes systems for supplying the inert solvent and disposing of the contaminated solvent. Inert gas taps should be provided in the transfer system as a means of completely purging the system. The design of the system should also include a suitable means of insulation or refrigeration (e.g., vacuum jacket, outer wall insulation, cooling jacket, etc.) to maintain the propellant temperature below its decomposition level.

4.4.2.2.2 Pipe and Fittings. Pipe and welding fittings are normally manufactured according to standard thickness and weight, as proposed by the American Standards Association. Adherence to these standards reduces unnecessary duplication in the manufacture of pipe and facilitates purchases in small lots.

Pipe wall thickness shall be determined by the formula given in Ref. 4.35, Section 2, Chapter 4, Paragraph 214 (-3).

$$t_m = \frac{P\ D}{2S + 0.8P} + C$$

where

P = maximum allowable operating pressure, psig

D = outside diameter, inches

t_m = minimum pipe wall thickness, inches

S = maximum allowable hoop stress, lb/sq in.

C = allowance for mechanical strength, threading, and/or corrosion, inches

NOTE: Allowance should be made for temperature, as required.

Most specifications to which mill pipe is normally obtained permit the minimum thickness to be 12.5 percent less than the nominal thickness specified. This under-tolerance must be considered to ensure that the minimum wall as obtained will meet the required thickness. As the ASA Code points out, this method of solution is applicable to the so-called thin-walled pipe in which the pipe wall thickness, $\underline{t}$, minus C (corrosion allowance in inches plus thread depth or groove depth) is less than 1/6 times the outside diameter. Where this ratio is exceeded, Paragraph 324 of Ref. 4.35 recommends the use of the Lame Formula plus the value C for determination of pipe wall thickness. The Lame Formula is:

$$\frac{(D^2 + d^2)}{(D^2 - d^2)} = \frac{S}{P}$$

where

D = outside diameter, inches

S = allowable tensile stress per Table 12 of Ref. 4.35

P = design pressure, psi

Materials that can be used for piping in service with B_2H_6 are any of those noted as compatible in Section 4.2 (provided the physical characteristics are adequate); however, the presently preferred materials are the AISI 300 series stainless steels.

Flared, welded, or flanged fittings are preferred. Threaded pipe fittings should be avoided as possible sources of fuel leakage; however, where they must be used, it is recommended that the tapered pipe threads be sealed with Teflon thread tape. All joints and fittings should be accessible for pressure and leak tests. Piping and equipment systems should be electrically bonded and grounded. Piping containing B_2H_6 shall be clearly identified.

4.4.2.2.3 Pipe Hangers and Supports. Pipe supports, hangers, anchors, guides, and braces should be designed to prevent excessive stresses, deflection, and motion in operation of the system, or too large a variation in loading with changes in temperature, and to guard against shock or resonance with imposed vibration and/or critical flow conditions. This includes the use of micarta sleeves for the low temperature service and Unistrut clamps for gas flow systems. Design and selection of the pipe supports should be in full accordance with Ref. 4.35, Section 6, Chapter I. Additional information is included in Ref. 4.36 through 4.41.

4.4.2.2.4 Standard Flanges for Pipe. Tables are found in Ref. 4.34 through 4.36, 4.40, 4.42, and 4.43 showing the allowable working pressure ratings of pipe flanges at various operating temperatures.

ASA-B-16.5 flanges consist of seven pressure classes, each identified by the primary operating pressure: 150, 300, 400, 600, 900, 1500, and 2500 pounds. These nominal pressure ratings are the ratings at an elevated temperature below which operating pressures higher than rated are allowable. Each pressure class contains a range of sizes and types. Within the same class, the allowable working pressure varies with the material and the operating temperature. Flange bolting materials should be in accordance with Ref. 4.35, Section 3, Paragraph 209.

Flanged connections should be utilized as follows:

1. All flange connections shall conform to ASA specifications (see Table 8, Ref. 4.35).
2. For pressures below 300 psi (150 pounds ASA), raised face flanges with serrated finish gasket faces shall be used.
3. For pressures above 300 psi (to 2500 pounds ASA), either tongue and groove or RTJ flanges should be used.
4. Any required gaskets should be of the approved type as designated in Section 4.4.2.10.

4.4.2.2.5 Expansion Joints and Flex Joints. Pipe line expansion joints and flex joints for B_2H_6 service shall be limited to the packless, bellows type. Where flow conditions permit, liners should not be used in the joints, as liners make proper cleaning and decontamination difficult. Where it is economically feasible, it is always more desirable to design a piping system with the inherent flexibility of the pipe itself in the form of loops or bends to offset excessive thermal movement and resulting high stresses. Where it is impossible, bellows-type joints, designed in accordance with good engineering practice (Ref. 4.44 and 4.45), are recommended. Other data are included in Ref. 4.37, 4.46, and 4.47. Particular care should be taken in the design and installation of flex joints in piping systems to avoid stress conditions which can cause failure; of prime concern is the positive elimination of torsional stress. For pressure use, the joints should be restrained in the linear direction; for flexing motion in one plane, pinned and gimbaled joints are available.

A corrugated, seamless hose of 304, 316, or other stainless steel, with open pitch construction and welded flanged ends is recommended as a flexible connection for B_2H_6 service. Flexible hose lines with Teflon, fitted with flanged connections, also have been successfully used.

4.4.2.2.6 Identification. Diborane piping should be identified in accordance with MIL-STD-101A(10). The primary warning color (band) is yellow. The secondary warning color (arrow or triangle) is brown.

4.4.2.3 Stainless-Steel Tubing and Fittings. Tubing and fittings of 300 series stainless steel are used almost exclusively for B_2H_6 systems. (For systems $>$2-inch diameters, the use of stainless-steel pipe with flanges and/or welded joints is recommended.) All systems designed with stainless-steel tubing should conform to MIL-T-8808A (for type 321) MIL-T-8606A (for type 347), or MIL-T-8504 (for type 304). Fittings should conform to AN or MS standards for flared tube fittings.

4.4.2.4 Shutoff Valves. Selection of valves for B_2H_6 service imposes certain design requirements that are more stringent or critical than with most other propellants. The primary considerations for selection are that the valves be leakproof and made of compatible materials. The design should be such that trapping of B_2H_6 in any part of the valve is impossible during any operation cycle of the valve. Nonlubricated valve designs acceptable for use with other toxic and corrosive liquids may be used with B_2H_6. Valves used with B_2H_6 must be thoroughly cleaned, inspected, and tested for leaks prior to installation and use.

Particle migration is a problem whenever valve parts rub, turn, or wedge on plastic sealing materials such as polychlorotrifluoroethylene or tetrafluoroethylene. This can cause problems in seal

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life such as plugging of minute orifices and instruments and fouling of close-tolerance fits. Migration is a particular problem in butterfly and soft-seated gate valves.

Plug, needle, and globe valves have been employed satisfactorily in B_2H_6 service. Table 4.11 provides a description of a 1-inch pneumatically actuated globe valve used successfully (Ref. 4.24) in liquid and gaseous B_2H_6 service. Leaks through the stem packing (tetrafluoroethylene) of this valve can be corrected by adjustment of a packing nut. Other users (Ref. 4.11) of B_2H_6 have indicated the use of a copper seat instead of the Teflon seat noted in Table 4.11.

4.4.2.5 Check Valves. As with shutoff valves, a variety of check valve designs exist which may be used in B_2H_6 service, depending upon system requirements. For sizes up to 2 inches, the aircraft-type, or in-line poppet check valve of stainless-steel construction with Teflon or Kel-F soft seat is recommended. For systems above 2 inches, any of the high-quality industrial-type valves of the swing check, poppet, or ball check designs are acceptable when constructed of compatible metals and seat materials. It is recommended that the normal cracking pressure of check valves be increased to provide positive seal in B_2H_6 service. Double check valves of the ball or poppet type with soft metal (copper) seats upstream and Teflon seats downstream have been used (Ref. 4.11) as an added safety measure.

4.4.2.6 Relief Devices. Any high-quality relief valve with good relief-reseat characteristics and bubble-tight shutoff upon reseat may be used. Again, such a valve should be of stainless-steel construction with Teflon or Kel-F seat. Valves made by Anderson-Greenwood (J-series), or equivalent, have been successfully used (Ref. 4.11) for this service. For use as an alternate relief device, rupture disks (burst disks), placed in parallel with the valve, are recommended. These disks are available in a wide

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variety of sizes, alloys, and burst ratings. These disks require special safety head flanges or holders, which are available in many materials and types for use in B_2H_6 systems.

Relief devices should be rated to burst at not more than 100 percent of the vessel or system rating when used as a primary relief device, or 105 percent when used as a secondary relief device. The relief devices must be sized to prevent the pressure from rising 10 percent above the maximum allowable working pressure.

4.4.2.7 Regulators. Regulators are primarily used to supply regulated inert gas (i.e., N_2 or He) for transfer, blanketing, purge, and control systems. The selection of regulators for service in B_2H_6 storage facilities depend upon its use. If a regulator is in a system which cannot be internally contaminated with B_2H_6, no special requirements are necessary. Where contamination is a possibility, the regulator material must be compatible and must have positive sealing characteristics. Because the normal regulator diaphragm material is not compatible with B_2H_6, the diaphragm can be protected by covering the exposed surface with a thin sheet of Teflon or Kel-F. Such modified regulators manufactured by Grove, Victor, Hoke, or equivalent have been used successfully.

4.4.2.8 Pumps. There is no acceptable pump available at present for B_2H_6 (Ref. 4.15).

4.4.2.9 Filters. Filters have an important role in B_2H_6 storage and transfer systems in maintaining propellant and inert gas cleanliness. Filters should be selected with woven wire mesh elements, fabricated of appropriate and compatible materials (stainless steel is preferred). The sintered-microsphere-type elements should be avoided because of difficulty in

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cleaning properly, and also because the microspheres become loosened in repeated cleaning operations, and disintegrate. Pleated-type elements properly supported are preferred; they provide a smaller filter for the same filter area.

The filter should be selected and located for easy and repeated opening and cleaning. The elements and case should be capable of supporting the full applied upstream pressure without damage because this condition can occur with a plugged filter. Filters should be sized, rated, and selected for low pressure drop at the rated flows. Ten-psig differential pressure is the recommended maximum differential across a clean set of elements. Twenty microns nominal is recommended as the largest port size for use in liquid propellant operation. Microporous filters have been used in gas service.

4.4.2.10 Gaskets. The selection of gaskets for B_2H_6 service should be based on the materials recommended in Section 4.2.2.1. Materials normally used as gaskets are Teflon, Kel-F, and JM-76 (particularly in low temperature service), although a number of other materials are available. Metal-containing gaskets are usually recommended for high pressure and vacuum systems; however, contact between dissimilar metals should be avoided to prevent galvanic corrosion. The use of certain elastomeric materials (from a compatible base material) as gaskets must be carefully considered and the formulation tested prior to use because the plasticizer or filler material may be incompatible.

4.4.2.11 Lubricants. The compatible lubricants for B_2H_6 service are given in Section 4.2.2.1. The absorption of small amounts of B_2H_6 by some of these compatible lubricants (e.g., Fluorolube FS and DC 33 silicone grease) should be considered in the handling of these materials.

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4.4.2.12 Instrumentation. In the design of instrumentation internal probes or sampling tubes for B_2H_6 storage and handling systems, the proper selection of compatible materials is the primary consideration. As noted previously, "dead ends," which are those places that could be filled with B_2H_6 without permitting adequate recirculation of the fluid, should be avoided wherever possible. (A common example of this in instrumentation design is the typical Bourdon-tube pressure gage.) The disadvantage of having a dead end in a piece of apparatus is that there is a possibility that contamination will accumulate in the dead end. If dead ends cannot be avoided, they should be placed above the low point in the system so that liquid B_2H_6 will not collect in them.

4.4.2.12.1 Liquid Level Indicators. Liquid level indicators for B_2H_6 storage or run tanks must be selected of compatible materials and preferably of the same alloy as the tank and piping. If external tank-sight gages are used, the gage valves should incorporate ball check valves for automatic liquid and vapor flow shutoff in case of gage breakage. The Jergenson sight gage has been used with liquid B_2H_6 (Ref. 4.11). Standard magnetic, float, and similar gages can be used in place of sight gages.

4.4.2.12.2 Pressure Gages. Pressure gages must be of approved materials and should have solid case front, blowout back, and be provided with a surge shutoff. To minimize operator reading errors, all pressure gages used for a common purpose should have identical scales. Pressure gages with stainless-steel Bourdon tubes have been used with proper precautions for draining.

4.4.2.12.3 Flowmeters. Cavitating venturi meters and turbine-type flowmeters have been used successfully for measuring B_2H_6 flowrates (Ref. 4.11).

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4.4.2.12.4 Temperature Measurement. Thermocouples or a platinum resistance bulb enclosed in a stainless-steel sheath or other similarly compatible material may be used for temperature measurement.

4.4.2.12.5 Air Pollution Monitoring. Several instruments are available for measuring or detecting B_2H_6 vapors in air. These units are described in Section 6.3.1.

4.4.3 System Fabrication and Assembly

Diborane storage and transfer systems are similar to those employed for handling ordinary fluids, except for materials of construction. Solenoid valves, electrical switchgear, and other electrical equipment in the B_2H_6 transfer and storage systems should be selected and installed in accordance with the requirements of the National Electric Code, Article 500, Class 1, Division 2. All seals and joints in the propellant system should be periodically and frequently inspected for leaks and damage.

In the layout, placement, and arrangement of operating systems and units, ample spacing should be provided for proper maintenance clearances and adequate ventilation. In many cases, the removal, replacement, and servicing of valves, pumps, piping sections, instrumentation, and other equipment must be done by workers in protective clothing and wearing respiratory equipment. Ample room and access must be provided for use of tools and for easy movement of equipment. Where possible, equipment, valves, and lines should be located so that maintenance and service work can be accomplished from a position above the piping level, to prevent propellant drips and leaks from falling on personnel.

Prior to fabrication and assembly of the system, the materials and equipment to be used should be carefully selected from the recommended lists as presented in Section 4.2.2 and 4.4.2. Any questionable or unknown (with respect to compatibility) material or piece of equipment, which is to be used in the system, should be thoroughly checked. In addition, the identity of each material used in the fabrication and assembly of systems must be ensured; test kits are available for the identification of metals in the field (Ref. 4.48).

These selections should be judiciously reviewed by knowledgeable personnel who have had prior experience in the operation of B_2H_6 facilities. The selected materials and equipment should be cleaned and passivated in accordance with Section 4.3 and the system should be fabricated and assembled according to the considerations presented in the following paragraphs.

4.4.3.1 Welding. In general, the standards for welding pipe will conform to Chapter 4 of Ref. 4.35. Pipe fittings should be procured from reputable sources who permanently mark their fittings as to: (1) manufacturer, (2) size and schedule of pipe, and (3) material and heat code. The fittings should be of the butt-welded type to facilitate system cleaning and purging operations. A typical set of standards for the acceptance of pipe welds is as follows:

1. Cracks of any nature, whether crater, underbead, transverse, longitudinal, or parent metal will be cause for rejection.
2. Crater cracks which are determined to be only surface defects may be removed by machining or grinding. They need not be rewelded provided buildup is not less than 10 percent or more than 30 percent of the metal thickness, or if drop-through is not less than flush or more than 30 percent of the metal thickness.

3. Normally acceptable defects occurring in conjunction with or adjacent to cracks will be cause for rejection if they occur within a distance 2 inches each way from the crack.

4. Butt joints will have 100-percent penetration throughout 100 percent of the linear length of the weld.

5. Any lack of fusion will not be accepted.

6. Undercut, excessive drop-through, and excessive roughness will be cause for rejection. Folds in drop-through will be accepted if they are not greater in depth than 10 percent of the thickness of the parent metal.

7. Porosity or inclusions occurring in the weld metal, exclusive of the weld reinforcements in which any radiographic image is darker than the parent metal or larger in its greatest dimension than 15 percent of the parent metal thickness, will be rejected.

8. Porosity and inclusions in the weld reinforcement will be acceptable provided they do not extend through the surface of the reinforcements and provided they do not result in an objectionable stress riser.

9. Porosity and inclusions whose greatest dimensions are equal to or less than 15 percent of the parent metal thickness will be acceptable to the extent of one pore per inch of weld length.

10. Tungsten inclusions located in the penetration zone will be accepted provided the greatest dimension of any particle is not over 25 percent of the parent metal thickness.

4.4.3.1.1 Stainless Steel. Fusion welding of stainless-steel pipe and fittings should be started with a root pass using the inert-gas-shielded tungsten arc method; helium or argon can be used as the inert gas. Subsequent passes may be made by the shielded metal-electrode method or by the inert-gas-shielded tungsten arc method. An inert gas (argon preferred) back-purge should be maintained during the welding of stainless-steel pipe and fittings until the weld area metal temperature falls below 400 F. Shielded electrodes shall conform to MIL-E-6844 and welding rods to MIL-R-5031. Additional information on the welding of stainless-steel pipes and fittings is presented in Ref. 4.35, 4.42 through 4.45, 4.49, and 4.50.

4.4.3.1.2 Aluminum. Because certain aluminum alloys may eventually be used (see Section 4.2.2.1) as pipe material for service with B_2H_6, some discussion on the welding of this material is included. Fusion welding of aluminum pipe and fittings can be accomplished by the inert-gas-shielded tungsten arc method or by the shielded metal-electrode method. These welding methods require a back-purge of inert gas. Detailed information on the welding of aluminum and aluminum alloys is presented in publications of the leading aluminum manufacturers (Kaiser, Reynolds, Alcoa, etc.).

4.4.3.2 Brazing and Soldering. Brazing and soldering techniques are not recommended for application in B_2H_6 systems. The joints produced by these methods may be incompatible (i.e., may cause B_2H_6 decomposition) with the propellant.

4.4.3.3 Mechanical Joints. The advantages of a relatively leak-free, all-welded transfer system are obvious. From a practical standpoint, however, some type of joint, whether flanged or otherwise, is required to facilitate maintenance and to provide adequate system flexibility.

Small valves and components should be selected with AN flared-type connections. Large valves and components should be selected with flanged connections. Instrumentation connections should be of the AN type, and can be provided by welding boss fittings on large pipelines or by installing tee fittings on small lines.

4.4.3.3.1 Threaded Pipe Joints. Threaded pipe joints should be avoided because these are a potential leakage source. In addition, localized corrosion may originate in this type of joint.

4.4.3.3.2 Flanged Pipe Joints. Flanged pipe joints are recommended whenever it is not practical to use welded joints. The flanges shall conform to ASA standards (Ref. 4.35, 4.36, and 4.51) for the welding neck type. Small tongue and groove, or raised-face flanges are preferred because most valves and pipeline components used in transfer systems can be furnished with these facings. A 1/8-inch-thick, full-face gasket of appropriate material is recommended for sealing the flanged joints. To ensure minimum distortion in welding these flanges to piping, a heavy backup plate or mating flange must be installed during welding operations.

4.4.3.3.3 Tube Connections. Standard and hand-polished flared tube connections are frequently used in B_2H_6 systems. This type of joint is particularly suitable for instrumentation sensing line connections. Copper conical seals have been used (Ref. 4.11) on flared connections for more positive seals.

4.4.3.4 Inspection. In the construction, installation, and modification of B_2H_6 systems, inspection is important to ensure quality of materials, adherence to design specifications, and proper fabrication techniques. Before installation, each piece of equipment, such as flex joints, valves, filters, etc., should be inspected and tested for:

1. Cleanliness
2. Proper lubricants (if allowable)
3. Leakage (internal and external)

4. Pressure-proof test
5. Sealant and gasket materials
6. Proper operation
7. Freedom from defects
8. Adherence to applicable specifications (type, size, rating, dimensions, etc.)

Piping and tubing sections should be inspected and tested for:

1. Conformance to design specifications and building codes
2. Identity and quality of materials of construction
3. Adequacy of supports; freedom from "cold spring"
4. Cleanliness
5. Proper fabrication workmanship
6. Proof-pressure and leak tests
7. Proper installation of flex joints

Electrical installations and equipment shall be inspected and tested for:

1. Conformance to design specifications and applicable codes
2. Adequate grounding
3. Insulation resistance
4. Circuitry continuity and proper termination
5. Workmanship and fabrication technique
6. Proper support of conduits and wiring

Instruments (flowmeters, gages, transducers, etc.) should be shop tested, calibrated, and certified with due regard to using conditions, fluid density, operating range, material identity, repeatability, and sealing capability. These instruments must be inspected for cleanliness prior to installation.

Roads, buildings, structures, etc., should be inspected for conformance to design specifications and building codes.

4.4.3.5 Radiographic Inspection

Items fabricated from standard pipe and fittings ordinarily have a sufficient factor of safety that radiographic inspection is not necessary. However, radiographic inspection may be required under the following conditions:

1. When noted on the governing drawing or specification; such is the case when it becomes necessary to obtain high weld efficiencies
2. When welds are visually suspicious; such as the case when the welder or the inspector doubts the soundness of the weld
3. When items are fabricated from nonstandard piping or fittings

Critical areas such as primary structures and anchor weldments, whose failure would result in installation or anchor collapse, shall be thoroughly analyzed by the designer and radiographic inspection specified, if required.

Radiographic inspection shall be specified only when it is beneficial. This type of inspection is not applicable to all weld types, and is a relatively costly process. Properly designed piping systems, welded by a certified welder and visually inspected by a qualified inspector, normally do not require radiographic inspection.

4.4.3.6 Hydrostatic and/or Pneumatic Tests. All components and tanks to be placed in B_2H_6 service should undergo applicable hydrostatic and/or pneumatic proof testing before they are cleaned and passivated.

> NOTE: Hydrostatic testing should be conducted with water.

After cleaning and chemical passivation, all proof and leak testing should be conducted only with deionized or distilled water, or with clean, filtered, hydrocarbon-free nitrogen gas or air. All components must be thoroughly dried before use with B_2H_6.

4.5 HANDLING

Because most B_2H_6 handling operations are specific to a particular system, the description of the operation cannot be treated with generalized criteria. Thus, B_2H_6 handling operations as described in this handbook are limited to operations which are common to all B_2H_6 facilities, such as cylinder handling, cylinder unloading, system and equipment decontamination, venting, and disposal operations. In addition, criteria that must be observed during all handling operations are reemphasized. Examples of detailed B_2H_6 handling particular to a variety of operations can be found in Ref. 4.4, 4.6, 4.10, 4.12, 4.23. 4.24, and 4.31. A number of additional references to this subject can be found in Sections 2.6, 2.7, and 3.1.

4.5.1 General Operating Criteria

All large-scale B_2H_6 handling operations should be conducted under meteorological monitoring and control. Specific operating procedures must be established for each handling operation, and personnel performing these handling operations should be completely familar with the nature of the operation and the procedures governing it. All operations involving propellant transfer or hazard control should be conducted by personnel wearing fully protective equipment as described in Section 6.4.1.2. The number of personnel conducting these operations should be limited to only those required for efficient performance of the operation; however, a minimum number of two personnel is always required.

4.5.1.1 Meteorological Concepts. The concept of establishing meteorological monitoring of activities capable of discharging toxic effluents into the atmosphere is well accepted. The precise nature of these activities, and the environment in which they are performed, determines the extent of meteorological control required.

Considering a storage and test complex as an entity, the contribution of the meteorologist is of the greatest importance in the planning and site selection phases. Working with the facility engineers, he must achieve a design and location which would guarantee that any release of toxic gases resulting from an accidental propellant spill of any conceivable magnitude would be reduced to relatively harmless concentrations by the time it reaches off-site population. These design and location criteria must be valid for the worst probable meteorological conditions.

It is obvious that when these protective criteria have been realized, there are no normal operational activities at a storage and test complex which could constitute any greater off-site hazard. In effect, this indicates that meteorological control is not required at the storage and test complex for the protection of off-site population.

To afford the maximum protection to operating personnel on or near the site, additional measures must be taken. Personnel exposure to toxic gases is minimized not only by proper and judicious use of safety clothing and breathing equipment, but also by:

1. The use of detection equipment in conjunction with alarm systems to warn of accidental releases.
2. The performance of transfer and disposal operations under specifications established by competent meteorologists. These specifications are dependent, for the most part, upon the specific orientation of buildings, roads, and offices, and would establish, primarily, the proper wind directions, wind speeds, and times of day for safe operation.

It is recognized that no storage area would be completely independent, but that it would exist in conjunction with either a rocket launch or test installation. It is at the latter facilities, where the probability of massive toxic releases is great, that a Meteorological Control Center would exist. The minor meteorological effort required for a storage area should be directed by this central control office.

Meteorological instrumentation required for a storage and test complex is basic, consisting of wind direction and speed transducers connected to recorders and hygrothermographs located in weather instrument shelters. The number and location of these instruments is a function of facility size and topography and is determined by the meteorologist as part of his site analysis.

4.5.1.2 Safety Procedures. All B_2H_6 handling should be conducted with full cognizance of the potential handling hazards and the hazard prevention, hazard control, and personnel protection procedures detailed in Section 6.

4.5.1.3 System Integrity. Diborane should only be handled in completely compatible and passivated systems under the criteria established previously in Section 4.1 through 4.4. ANY CONTAMINATION BY MOISTURE, AIR, SOME SOLVENTS, ETC., OF THE PASSIVATED SYSTEM MUST BE PREVENTED. If the system is contaminated or a new component (which should be clean and chemically passivated) is placed into the system, the affected parts exposed to contamination should be repassivated prior to use (refer to Section 4.3.1).

4.5.2 Handling of Shipping Container (See Section 5.4.1)

The shipping cylinders must be handled with extreme care. The cylinder shutoff valve(s) cap(s) must be installed at all times during cylinder handling operations. The cylinders may be transferred by means of any piece of equipment capable of handling them safely. While in transfer, the cylinders must be firmly secured. Storage of the shipping cylinders should be restricted to those areas specifically designated for this purpose. The condition of each cylinder (full, empty, contaminated, etc.) must be marked clearly.

It is essential that any full or partially full shipping containers be refrigerated to prevent decomposition of the B_2H_6. Techniques are described in Section 5.4.1. If the shipping containers are stored in an ice chest or box, care should be taken to prevent ice accumulation on the containers, and that they are not permitted to become frozen in place. Because the steel of the container is brittle when cold, B_2H_6 should not be stored at less than -80 C (-108 F), and even at that temperature, precautions should be taken to ensure that the cylinder is not bumped and sudden pressure surges do not occur (Ref. 4.1).

Diborane containers should always be kept at greater than atmospheric pressure to prevent the possibility of air leakage into the container and resulting formation of an explosive B_2H_6-oxygen mixture. Accordingly, the pressure in the storage cylinder should never be allowed to fall below 30 psig at room temperature, so that the pressure at 80 C (-108 F), upon subsequent storage, would not be below atmospheric pressure. If this occurs, a dry inert gas or hydrogen gas can be added to maintain 30 psig (Ref. 4.1).

All open flames, sparks, heat, and other sources of ignition should be kept away from areas where B_2H_6 shipping cylinders are handled or stored.

Empty cylinders should never be refilled or used for the storage of other chemicals. They should be flushed with dry nitrogen for five (5) minutes to insure that essentially all the B_2H_6 has been removed, and then pressurized to 25 psig. The valve outlet cap must be replaced and closed securely, and the valve protection cap replaced before the containers are offered for the return shipment. The lower portion of the ICC combination label shipping tag, if attached to the cylinder, must be removed. If boxed cylinders are returned in original shipping cases, the ICC label on the outside package must be removed, defaced, obliterated or covered by the prescribed white ICC "Empty" label (Ref. 4.1).

4.5.3 Transfer of B_2H_6 From Shipping Container

Diborane can be discharged from its storage container either by its own vapor or gas pressure, or by pressurizing the container with dry nitrogen or helium. Inert gas pressurization is used almost exclusively at the present time for unloading large amounts of liquid B_2H_6, because this technique is extremely reliable. Vapor pressure unloading is used primarily in the transfer of small quantities of liquid or gaseous B_2H_6.

The transfer system must be chemically compatible with B_2H_6, leak-proof, and in excellent operating order. The complete system must also be completely passivated, dried, and purged with dry nitrogen or helium gas prior to the commencement of complete flow conditions. It should be maintained free of air, moisture, and other contamination.

In preparing for a transfer operation, all personnel not directly concerned with the operation shall evacuate the hazard area. Appropriate warning lights and signs shall be displayed to keep out unauthorized personnel. Personnel performing the transfer operation shall wear the fully protective equipment described in Section 6.4.1.2. If the operations are performed remotely, at least two operating personnel should be fully dressed to facilitate proper spill and fire control. Sufficient safety equipment should be available for all personnel allowed to remain in the hazard area. Supervisory and emergency support personnel shall be notified prior to executing any hazardous operation in the storage area.

The propellant transfer procedures are dependent upon numerous factors such as transfer system design, type of propellant container, training of operating personnel, prevailing weather conditions, etc. Establishing proper operating procedures for each specific situation in a single document is not feasible. Therefore, the procedures suggested in the following paragraphs are general in nature. The transfer system schematic presented (Fig. 4.5) is not a finalized or complete design (e.g., pressure gages, thermocouples, filters, check valves, etc., which are required, are not illustrated); it is provided only to facilitate the explanation of typical procedures. The procedures are as follows.

4.5.3.1 Transfer of Liquid by Inert Gas Pressurization. As mentioned previously, the transfer of liquid B_2H_6 from the shipping cylinders can be accomplished reliably by pressurizing the cylinders with a dry inert gas. It was also mentioned elsewhere that dry helium is the inert gas presently recommended for these applications (because of high N_2 gas solubility in B_2H_6).

The following procedure is basically applicable to the pressurization unloading of liquid B_2H_6 from a shipping cylinder into a storage tank (refer to Fig. 4.5):

1. Position and secure the cylinder.
2. Ensure that all the system valves are closed, except for valve No. 11 which must be maintained open. The object of valve No. 11 is to facilitate the removal of the burst diaphragm whenever required.
3. Connect the cylinder shutoff valves to the transfer system as shown in Fig. 4.5.
4. Set the inert gas regulator to the desired pressure. This pressure level determines the propellant discharge flow. A value ranging from 25 to 50 psig above the

cylinder pressure should be adequate. This also assumes that the temperature of the shipping cylinder is at or slightly above the temperature of the storage tank (ideally about -108 F). In any case, the pressure should never exceed 10 psig less than the container design pressure.

5. Purge the propellant lines to remove trapped air and water vapor. This can be accomplished as follows:

   a. Open valves No. 1 and 2, and purge for about 3 minutes.

   b. Close valve No. 2 and 1.

   c. Open valves No. 7 and 3, and purge for about 3 minutes (vent the solvent catch tank as required).

   d. Close valve No. 3.

   e. Open valves No. 5 and 2, and purge for about 3 minutes with the connections loosened at valves No. 4, 6, and 8.

   f. Tighten all connections and close valves No. 2, 5, and 7.

   NOTE: The above procedure assumes that the storage tank contains B_2H_6 or it has been serviced for B_2H_6 and contains an inert gas blanket, thus requiring no purging.

6. Start the B_2H_6 transfer by slowly opening valves No. 8, 6, 4, and 1.

7. When the desired quantity or all of the available B_2H_6 has been transferred, close valves No. 6 and 1.

   NOTE: There are several devices which can be used to detect the completion of the propellant transfer operation. Combinations of two or more devices are usually required to provide the desired transfer system flexibility. Some of these devices are: (a) a flowmeter installed in transfer line; (b) a scale or other weight-sensing device attached to the cylinder being unloaded; or (c) a calibrated level indicator mounted on the storage tank.

8. Vent the B_2H_6 cylinder by opening valve No. 2 momentarily until the container pressure is about 15 psig at -108 F

9. Close valve No. 4

10. Open valves No. 1 and 5, and purge the transfer line for about 5 minutes.

> NOTE: If the storage tank pressure equalizes the purge pressure before the purging operation is completed, close valve No. 8, and open valve No. 10 momentarily until the pressure drops to about 15 psig (assuming a storage tank temperature of -108 F). The purge operation is resumed by reopening valve No. 8.

11. Close valves No. 1, 5, and 8.

12. Vent the storage tank to about 15 psig by opening valve No. 10 momentarily.

13. Purge the transfer line with an inert solvent (kerosene - see Section 4.5.4) by opening valves No. 9 and 3 for about 3 to 5 minutes.

14. Close valve No. 9

15. Open valve No. 7 and purge for about 3 to 5 minutes

16. Close valves No. 7 and 3.

17. Purge the B_2H_6 cylinder vent line for about 3 minutes by opening valves No. 1 and 2.

18. Close valves No. 1 and 2.

19. Disconnect the shipping-cylinder shutoff-valves from the transfer system and cap the opened components. (As described previously, a CO_2 fire extinguisher can be of great value while performing this step.)

20. Mark and dispose of the shipping cylinder according to operating procedures.

21. Notify all personnel concerned that the transfer operation is completed and the area clear.

> NOTE: If it is not necessary to remove the shipping cylinder or any system components, steps No. 13, 14, 15, 16, 17, 18, 19, and 20 can be omitted except that the cylinder must be marked adequately.

4.5.3.2 Transfer of Liquid by Vapor Pressure. The transfer of liquid B_2H_6 from the shipping cylinder can be accomplished by its own vapor pressure, but this technique is less reliable and may result in some decomposition of the B_2H_6. In this procedure, the steps are essentially the same as those noted in Section 4.5.3 except for the following additions and eliminations:

1. Between steps 5 and 6, the B_2H_6 shipping cylinder should be allowed to warm up by removing the temperature conditioning fluid.
2. In step 6, valves No. 4 and 1 should remain closed.
3. Between steps 7 and 8, the shipping cylinder should be reconditioned to its original temperature.
4. In step 8, the shipping cylinder is vented by opening valves No. 4 and 2.

4.5.3.3 Transfer of Gas. The transfer of small amounts of gaseous B_2H_6 from the shipping cylinder can be accomplished in a similar manner. Using a transfer assembly similar to that shown in Fig. 4.5 (except that a connection is not necessary at valve No. 6), the procedure is similar to that of Section 4.5.3.1 except for the following additions and eliminations:

1. Between steps 5 and 6 the B_2H_6 shipping cylinder should be allowed to warm up by removing the temperature conditioning fluid.

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2. In step 6, the transfer is initiated by slowly opening valves No. 8, 5, and 4. Valves No. 1 and 6 should remain closed.
3. In step 7, the transfer is stopped by closing valves No. 4 and 5.
4. Between steps 7 and 8, the shipping cylinder should be reconditioned to its original temperature level.

4.5.4 Equipment and System Decontamination

Any system and all equipment which has been used in B_2H_6 service must be thoroughly decontaminated prior to performance of system maintenance, replacement of components, its preparation for inactive storage, or its use in other service. The decontamination steps are designed to remove all residual B_2H_6 and higher boranes (from B_2H_6 decomposition), so that it can be handled safely with no possibility of fire and explosion from reactions with air and/or of personnel intoxication.

> WARNING
>
> Personnel protective clothing and respiratory protection per Section 6.4.1.2 must be worn during the decontamination procedures until the operation is complete.

A general recommended procedure for decontamination of systems and equipment in B_2H_6 service has been reported in Ref. 4.2 as follows:

1. Transfer residual B_2H_6 from the system into closed refrigerated containers (using a technique similar to that described in Section 4.5.3) such as the original shipping cylinders or dispose of it using a prescribed procedure

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(see Section 4.5.6). Purge the vessels or system with a dry inert gas, such as nitrogen or helium, flaring or scrubbing the vent gases (see Section 4.5.5) to eliminate the fire and intoxication hazard.

> NOTE: If a component is to be removed and it can be isolated from the system (a consideration to be noted in the design of the system), then only the isolated section has to be decontaminated.

2. Fill the vessel, system, or section being decontaminated with water-free kerosene and drain. An auxiliary tank for handling this kerosene is useful in large-scale operations, otherwise drain the kerosene into drums. The kerosene contains dissolved or slurried boron materials and must be treated carefully as it is toxic. The drums must be stored in a safe area with a loose bung to prevent overpressurization. If there is no shelter to prevent rain from entering through the loose bung, a gooseneck must be used. Respiratory protection must be worn when handling these drums. After several usages, the kerosene will become useless for further decontamination and must be destroyed by incineration.

3. The vessel, system, or section is then filled with cold water to react with any residues. The operation must be performed slowly, and remotely if practical, with ample venting capacity provided to dispose of the hydrogen evolved by hydrolysis of the product. After draining, the system is refilled with cold water. This is repeated until the effluent is clear, indicating that decontamination is almost complete. A final steaming will destroy any residual fuels, after which the equipment may be safely opened with due caution.

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4. After completing decontamination, certain parts such as valves, compressor packings, filter cartridges, etc., may still contain boron compounds. These components should be immersed in a 10 percent aqueous solution of methanol as they are removed from the system and then steamed.

5. Following all decontamination, the vessel, system, or section should be completely dried. This may be accomplished by heated purges with dry inert gas or by several rinses with acetone followed by heated purges with dry inert gas.

All combustible liquids containing boron compounds must be incinerated. These solutions must be treated as toxic material. The incineration of boron materials generates boron oxide which, while not toxic to humans (on the basis of animal studies), may be objectionable when discharged into the air and, in specific instances, may be toxic to certain vegetation. Therefore, the combustion products should be scrubbed to remove the boron oxide. Hot water or steam as scrubbing medium will facilitate the separation of the boron oxide from the combustion products.

4.5.5 Venting

During various system operations (depressurizing, loading, disposal, etc.), venting of B_2H_6 gas or vapors is frequently required. In this venting operation, a significant amount of B_2H_6 may be released, and it must be disposed of in a safe manner. Three basic methods can be utilized to dispose of vented B_2H_6 vapor or gas. These methods are:

1. The transfer system vent lines can be connected to a vapor scrubber system which removes the B_2H_6 vapor from the vented gases. The scrubber system operation consists of reacting the B_2H_6 with an adequate chemical (alcohol, ammonia, etc.) in solution before the gases are released

to the atmosphere. The remaining solution becomes in turn contaminated and must be disposed of by incineration. In addition, because the reaction of these chemicals usually produces H_2 gas, the vent gas should be passed through a flare system after passing through the scrubber. (An illustration of a methanol-water scrubber, given in Ref. 4.24, is presented in Fig. 4.6).

2. The transfer system vent lines can be connected to a high vent stack which discharges the vented gases at least 75 feet from the highest working point in the area. An inert gas purge should be installed in the stack to further dilute the vented B_2H_6 vapor. The vent lines shall be terminated with an appropriate flame arrestor to prevent the possibility of B_2H_6 combustion flashback. (This technique should only be used in isolated areas for very small amounts of B_2H_6 gas.)
3. The transfer system vent lines can be connected to a flare system which burns the B_2H_6 vapor before being released to the atmosphere. The flare system must be equipped also with an appropriate flame arrestor to prevent flashback.

Diborane containers and systems should be vented only under controlled conditions. These conditions are dependent upon area location, prevailing weather, method of disposing of vented B_2H_6 vapor, etc.

4.5.6 Disposal

The disposal of stored B_2H_6 or contaminated solvent can be performed efficiently by incineration. This operation can be performed in a properly designed burn basin (with a smooth and impervious cement or metal lining) equipped with a reliable ignition device.

The following items are essential for the proper selection and safe operation of the B_2H_6 disposal area:

1. The disposal area shall be isolated in accordance with the quantity-distance tables presented in Section 4.4.1.1.2.
2. The disposal area shall be clear of trees, weeds, brush, and other combustibles.
3. The area must be equipped with adequate safety equipment (see Section 6.4.1).
4. The personal safety equipment, described in Section 6.4.1.2, must be worn during disposal operations.
5. One person shall never be allowed to work in the disposal area alone.
6. All personnel not participating in the disposal operation shall evacuate the area.
7. Disposal operations shall be performed only under controlled conditions. The disposal of B_2H_6 can be accomplished initially by placing several gallons of inert solvent in the burn basin and setting the solvent afire. The propellant is then fed slowly into the basin and allowed to burn with the solvent. For this operation, the B_2H_6 container should be located at least 50 feet from the burn basin.

Contaminated solvent can be disposed of by feeding it to the burn basin and setting it afire.

An example of a system and procedure for disposal of residual B_2H_6 from full or partially filled shipping cylinders, as given in Ref. 4.1, is as follows:

1. Set up lines and valves as shown in Fig. 4.7, allowing about 50 feet of clean copper tubing from gas outlet to burning pan.

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2. Do not tighten connections at closed valves No. 1 and 2.
3. Open nitrogen cylinder valve, set regulator to 15 to 20 psig and allow nitrogen to sweep through loose connection valves at 1 and 2, and through open valve No. 3. Resistance to gas flow in the 50 feet length of tubing will allow nitrogen to purge loose fitting at valve No. 2.
4. Tighten fittings at valves No. 1 and 2, close valve No. 3.
5. Ignite burning pan containing a small amount of kerosene.
6. Crack gas outlet valve No. 2 and slowly bleed B_2H_6 into burning pan.
7. Observe the burning flame of the B_2H_6. Check the open end of the flare tube to be sure it is not crusted over with boric oxide. If it is open and the flare dies down, this indicates that the cylinder pressure is almost exhausted. Carefully open dip leg valve No. 1 and admit nitrogen sweep to cylinder and out valve No. 2 to burning pan.
8. As B_2H_6 becomes more dilute, flame will change from green-orange to a blue and finally go out from lack of fuel. Cylinder may then be considered safe to ship.

   NOTE: Check open end of copper tubing to be sure that it is not crusted over and impeding gas flow.

9. Close valve No. 2, allow nitrogen to build up in cylinder, to preset regulator pressure (15 to 20 psig) and close valve No. 1.
10. Remove lines, replace caps on valves No. 1 and 2, and return cylinder to crate.

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TABLE 4.

SUMMARY OF B_2H_6 STORA

B_2H_6 Sample		Container		Test Condi		
Phase	Quantity, cc	Material Type	Volume, ml	Ullage, v/o	Temperature, F	Con
Liquid/Vapor	1.2 at -108 F	6061-T6 Al	6	~80*	-108	6061-T6 Specime
Liquid/Vapor	1.2 at -108 F	347 SS	6	~80*	-108	347 SS Specime
Liquid/Vapor	1.2 at -108 F	6Al-4V-Ti	6	~80*	-108	6Al-4V- Specime
Liquid/Vapor	2.0 at -108 F	347 SS	6	~33*	-108	Stainle Oxides (Specime
Liquid/Vapor	2.8 at -108 F	SS	14	80	-108	Irradia [10^9 er
Liquid/Vapor	7.4 at -108 F	SS	14	47	-108	Irradia [10^9 er
Liquid/Vapor	11.2 at -108 F	SS	14	20	-108	Irradia [10^9 er
Liquid/Vapor	NR**	Mild-steel shipping container		NR	-27.4	N
Liquid/Vapor	100 g	SS	500	~35*	-4	N
Liquid/Vapor	1.2 at -4 F	347 SS	6	~80*	-4	Stainles Oxides (Specimen
Liquid/Vapor	NR	Mild-steel shipping container		NR	0	N
Liquid/Vapor	10.5 at mp	SS	43	~55*	32	N
Gas	12.8 at mp	SS	115	-	32	N
Liquid/Vapor	NR	Mild-steel shipping container		NR	44.6	N
Liquid/Vapor	NR	Mild-steel shipping container		NR	60.8	N
Gas	NR	Mild-steel shipping container		-	77	N
Gas	6.7 at mp	SS	43	-	77	N

*Calculated data
**NR - Not reported

1

BILITY TESTS

tions		Results		
ditioning	Storage Time	Pressure Rise, psi	B_2H_6 Decomposition, m/o	Ref.
Al Corrosion n	45 days	NR**	See Table 4.3	4.8
Corrosion n	45 days	NR	See Table 4.3	4.8
Ti Corrosion n	45 days	NR	See Table 4.3	4.8
ss Steel Corrosion n	30 days	NR	See Table 4.3a	4.8
ted /g(C)]	NR days	22 7.5 (control) (see Table 4.4)	0.1 0 (control)	4.9
ted /g(C)]	NR days	15.1 0 (control)	0 0 (control)	4.9
ted /g(C)]	NR days	23.0 0 (control)	0.1 <0.1 (control)	4.9
one	100 days	0.003*	NR	4.5
one	13.5 months	~10 (see Table 4.2)	0.14*	4.7
s-Steel Corrosion n	30 days	NR	See Table 4.3a	4.8
one	100 days	2.06*	NR	4.5
one	197 days	0	NR	4.6
one	3 months	11	NR	4.6
one	100 days	~15*	NR	4.5
one	100 days	~90*	10	4.5
one	4 months	764	40 to 60	4.5
one	4 months	480 (see Fig. 4.3)	40 to 50	4.6

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TABLE 4.2

STORAGE OF B_2H_6 AT A NOMINAL TEMPERATURE OF -20 C (-4 F) IN STAINLESS STEEL (REF. 4.7)

Date	Temperature, C	Pressure, psia
1950		
11-29	-20	220
12-5	-20	223
12-13	-20	224
12-20	-20	224
12-27	-20	224
(Left at -30 C during 12-27-50 to 1-22-51)		
1951		
1-24	-20	224
1-30	-20	225
2-7	-20	225
2-14	-20	224
2-21	-20	224
2-28	-20	-
3-8	-20	227
4-4	-20	223
4-11	--	208
4-18	-20	213
4-25	-20	220
5-2	--	214
5-9	-24	208
5-16	-24	215
5-23	-27	187
5-29	-20	217
6-6	-20	223
6-13	-19	233
6-20	-30	158
6-27	-25	155
7-3	-30	135
7-11	-33	133
7-18	--	165
7-25	-25	192
8-1	-22	225
8-8	-23	180
8-15	--	198
8-22	-24	208
8-29	-30	180
9-5	-20	182
9-12	--	155
9-19	-25	160
9-26	--	127
10-3	-40	112
10-10	-30	150
10-17	--	250
10-24	-20	243
10-31	-20	240
11-21	-20	237
11-28	-21	235
12-5	-20	238
12-12	-21	224
12-19	-21.5	233
12-26	-24	222
1952		
1-2	-22	213
1-8	-20	236
1-16	-22	232
(The diborane was maintained at -30 to -40 C from 1-16-52 until it was assayed).		

TABLE 4.3

MASS SPECTROMETER ANALYSES OF B_2H_6 AFTER 45 DAY STORAGE AT -78 C (-108 F) (REF. 4.8)

Constituent	Shipping* Cylinder Analysis	Diborane in Contact With		
		6061-T6 Aluminum	347 SS	Titanium
Diborane, m/o	94.53	98.87	97.59	98.44
Hydrogen, m/o	3.63	0.18	1.81	0.47
Nitrogen, m/o	0.31	0.28	0.25	0.16
Oxygen, m/o	0.00	0.04	0.02	0.05
Hydrocarbons (as Butene),**m/o	0.79	0.23	0.17	0.26
Carbon Dioxide, m/o	0.10	0.07	0.07	-
Isopropoxypentaborane, m/o	0.64	0.23	0.09	0.09

*Callery Chemical Company B_2H_6 was stored in original shipping cylinder at -20 C (-4 F) for 1 year prior to analysis; the B_2H_6 used in the tests, which was purified by the transfer sequence, was not analyzed prior to the tests.

**The hydrocarbons were reported as butene rather than identifying the individual hydrocarbon molecules; butenes are perhaps fragments of higher molecular weight hydrocarbons.

TABLE 4.3a

MASS SPECTROMETER ANALYSES OF B_2H_6 AFTER 30 DAY STORAGE IN CONTACT WITH STAINLESS STEEL OXIDES (REF. 4.8)

Constituent	-20 C (-4 F)	-78 C (-108 F)
Diborane, m/o	97.5	98.35
Hydrogen, m/o	4.24	1.60
Hydrocarbons (as Butene), m/o	0.03	0.05

TABLE 4.4

RADIOLYSIS EFFECTS ON B_2H_6 STORED IN STAINLESS STEEL AT -108 F (-78 C) (REF. 4.9)

Sample	Ullage, percent	Exposure*	Phase	Analysis**				Pressure, Rise, psi
				H_2, μ-mole/g	B_2H_6, m/o	B_4H_{10}, m/o	B_5H_9, m/o	
8-80-3-C-G	80	Control	gas	5	-	NT	NT	7.5
8-80-3-C-L	80	Control	liquid	NT	100	NT	NT	-
8-80-2-R-G	80	Irradiated	gas	20	-	NT	NT	22.0
8-80-2-R-L	80	Irradiated	liquid	NT	99.9	0.1	NT	-
8-80-1-R-G	80	Irradiated	gas	18	-	NT	NT	22.0
8-80-1-R-L	80	Irradiated	liquid	NT	99.9	0.1	NT	-
8-20-1-C-G	47	Control	gas	6	-	NT	NT	0
8-20-1-C-L	47	Control	liquid	NT	100	NT	NT	-
8-20-1-R-G	47	Irradiated	gas	12	-	NT	NT	15.2
8-20-1-R-L	47	Irradiated	liquid	NT	100	NT	NT	-
8-20-2-R-G	47	Irradiated	gas	10	-	NT	NT	15.0
8-20-2-R-L	47	Irradiated	liquid	NT	100	NT	NT	-
80-20-1-C-G	20	Control	gas	30	-	-	-	0
80-20-1-C-L	20	Control	liquid	-	99.9+	TR	NT	-
80-20-1-R-G	20	Irradiated	gas	50	-	-	-	22
80-20-1-R-L	20	Irradiated	liquid	-	99.9	0.1	NT	-
80-20-2-R-G	20	Irradiated	gas	60	-	-	-	24
80-20-2-R-L	20	Irradiated	liquid	-	99.9	0.1	NT	-

*Either irradiated with a dose level of 10^9 erg/g (C) or a control (no irradiation).

**NT - no trace found; TR - trace quantity, <0.05 m/o

TABLE 4.5

SUMMARY OF MATERIALS COMPATIBILITY TESTS WITH GASEOUS B_2H_6 AT ROOM TEMPERATURE AND ATMOSPHERIC PRESSURE (REF. 4.6)

Material Tested	Time of Contact With B_2H_6	Observed Effect
Saran	72 hours	No observable effect.
Plastic sheet, composed of 50-50 polyethylene-polyisobutylene	24 hours	No observable effect.
DC 33 silicone low-temperature grease, consistency light 140A	24 hours	Somewhat lighter in color; otherwise unaffected. Absorbed a small amount of B_2H_6. Produced a slight amount of H_2 when water was added.
Half hard brass sheet	44 hours	No observable effect.
Lead sheet	99 hours	No observable effect.
Nickel shavings	72 hours	No observable effect.
Fluorolube FS (Hooker Electrochemical Co.)	72 hours	Some B_2H_6 absorbed. Found 0.028-percent B_2H_6 dissolved in fluorolube.
K-Monel	72 hours	No observable effect.
Kel-F sheet	96 hours	No observable effect.

TABLE 4.6

RESULTS FROM IRRADIATION* OF NYLON AND KEL-F SEALS IN CONTACT WITH B_2H_6 AT -108 F (-78 C) (REF. 4.9)

Seal Composition	B_2H_6 Lost,** percent	O-Ring Weight Change, percent	Initial Compression Set, percent	Seal Leaks Detected, std cc/min	Remarks
Nylon	6.4	+0.04	12.0 ±1.1	None	Rings turned yellow
Kel-F (plastic)	6.4	-0.04	9.5 ±1.4	None	--

Properties	Nylon	Kel-F (plastic)
<u>Pre-Exposure (Average)</u>		
Weight, g	0.4279	0.7884
Thickness, inch	0.104	0.106
Ultimate Stress, psi	10,502	5,366
Percent Elongation	47.6	46.4
Hardness (Shore "B")	82	80
<u>Post-Exposure (Average)</u>		
Weight, g	0.4281	0.7881
Thickness, inch	0.093	0.097
Ultimate Stress, psi	12,453	5,858
Percent Elongation	47.3	34.4
Hardness (Shore "B")	83	80

*Dose level of 10^9 erg/g (C)
**Apparently caused in filling operation

TABLE 4.7

RESULTS OF ELASTOMETER COMPATIBILITY AND PERMEABILITY TESTS WITH B_2H_6 (REF. 4.12)

Unfilled Cured Elastomer Compatibility Tests

Formulation	Propellant[a]	Sample Appearance	Weight Change, percent	Tensile,[b] percent	Elongation,[b] percent	Hardness,[c] percent
Tested in B_2H_6 at -78.5 C (-109 F)						
3-2, Nordel 1145 EPT	No change	Sw. swollen	-0.09	-50	-63	+4.1
3-1, HYCAR 1072 Nitrile	No change	No change	±0.15	+23	-27	+1.8
4-4, W-970 Silicone	No change	Swollen	>10	Not tested	Not tested	Not tested
Tested in B_2H_6 at 0 C (32 F)						
3-1, HYCAR 1072 Nitrile	No change	No change	Nil	+23	-12	+2
3-2, Nordel 1145 EPT	No change	No change	+0.16	-63	-94	+8
4-4, W-970 Silicone	No change	Swollen	>10	Not tested	Not tested	Not tested
Filled, Cured Elastometer Compatibility Tests at 78.5 C (109 F)						
10-2, CIS-4 Polybutadiene/Silica	No change	No change	+0.14	-77	-93	±0
10-1, W-970 Silicone/Silica	No change	Swollen	>10	Not tested	Not tested	Not tested
34-2, HYCAR 1072 Nitrile/Silica	No change	No change	+0.04	+0	+2.5	-3

Elastomer Permeability Tests

Composition[d]	Gas	Temperature C	Temperature F	ΔP, psia	Time, hours	P x 10^{10}[e]
HYCAR 1072 Nitrile	Helium	-20	-4	315	88	0.7
	B_2H_6	-20	-4	235	138	7.6
HYCAR 1072 Nitrile/Silica	Helium	-20	-4	315	49	0.5
	B_2H_6	-20	-4	255	130	9.1

[a] The infrared spectra of pretest and posttest propellant were compared. No new peaks or loss of old peaks were found.

[b] Microtensile die tested at 20 in./min crosshead speed at 23 C (73.4 F).

[c] Rex hardness units, very similar to Shore A.

[d] Nominal membrane size used was a 1.0-inch-diameter circle, 0.085-inch thick.

[e] Units = (cc STP) (cm)/(cm^2)-(sec)-(cm Hg)

TABLE 4.8

RESULTS OF CORROSIVITY TESTS ON METAL SPECIMENS STORED IN B_2H_6 (REF. 4.8)

Material	Bomb	Propellant Temperature	Storage Period, Days	Propellant Change	Material Change		
					Thickness Change, inch	Weight Change, mg	Surface Appearance
Ti-6Al-4V	Ti-6Al-4V	-108	45	See Table 4.3	+0.0001	nil	Slightly brightened from control specimen, minimal attack.
SS 347	SS 347	-108	45	↓	-0.0002	nil	Unaltered in appearance; relatively unaffected with very minor pitting.
Al 6061-T6	Al 6061-T6	-108	45	↓	-0.0004	-0.5	Surface brightened in appearance; minor pitting in both longitudinal and transverse direction.
Stainless Steel Oxides (304 SS combusted in O_2 (g))	SS 347	-108	30	See Table 4.3a	Surface fissuring of larger particles and a greater number of smaller particles indicating sample breakup; reduction of some of the oxide concluded.		
		-4	30	↓	Half of sample fused with considerable amounts of smaller particles; reduction of some of the oxide concluded.		

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TABLE 4.9

QUANTITY-DISTANCE STANDARDS FOR HAZARD GROUP III PROPELLANTS (REF. 4.15)

Pounds of Propellant		Inhabited Buildings Railroads, Highways, and Incompatible Group III Storage, distance in feet		Intragroup (Intraline) and Compatible Group III Storage, distance in feet
Over	Not Over	Unprotected	Protected	
0	100	600	80	30
100	200	600	100	35
200	300	600	110	40
300	400	600	120	45
400	500	600	130	50
500	600	600	135	50
600	700	600	140	55
700	800	600	145	55
800	900	600	150	60
900	1,000	600	150	60
1,000	2,000	600	175	65
2,000	3,000	600	190	70
3,000	4,000	600	200	75
4,000	5,000	600	210	80
5,000	6,000	600	220	80
6,000	7,000	600	225	85
7,000	8,000	600	230	85
8,000	9,000	600	235	90
9,000	10,000	600	240	90
10,000	15,000	1,200	260	95
15,000	20,000	1,200	275	100
20,000	25,000	1,200	285	105
25,000	30,000	1,200	295	110
30,000	35,000	1,200	300	110
35,000	40,000	1,200	310	115
40,000	45,000	1,200	315	120
45,000	50,000	1,200	320	120
50,000	60,000	1,200	330	125
60,000	70,000	1,200	340	130
70,000	80,000	1,200	350	130
80,000	90,000	1,200	360	135
90,000	100,000	1,200	365	135
100,000	125,000	1,800	380	140
125,000	150,000	1,800	395	145
150,000	175,000	1,800	405	150
175,000	200,000	1,800	415	155
200,000	250,000	1,800	425	160
250,000	300,000	1,800	440	165
300,000	350,000	1,800	455	170
350,000	400,000	1,800	465	175
400,000	450,000	1,800	475	180
450,000	500,000	1,800	485	180
500,000	600,000	1,800	500	185
600,000	700,000	1,800	515	190
700,000	800,000	1,800	530	195
800,000	900,000	1,800	540	200
900,00	1,000,000	1,800	550	205
1,000,000	2,000,000	1,800	630	235
2,000,000	3,000,000	1,800	675	255
3,000,000	4,000,000	1,800	710	265
4,000,000	5,000,000	1,800	740	275
5,000,000	6,000,000	1,800	760	285
6,000,000	7,000,000	1,800	780	295
7,000,000	8,000,000	1,800	800	300
8,000,000	9,000,000	1,800	815	305
9,000,000	10,000,000	1,800	830	310

TABLE 4.10

LIQUID PROPELLANT STORAGE COMPATIBILITY CHART (REF. 4.15)

Propellant	The Alcohols	Anhydrous Ammonia	Aniline	The Boranes	Ethylene Oxide	Fluorine and Fluorine-Oxygen Mixtures	The Halogen Fluorides	Hydrazine and Monomethylhydrazine	UDMH and Mixed Amine Fuels	Hydrocarbon Fuels	Hydrogen, Liquid	Hydrogen Peroxide	Methane, Liquid or Gas	Nitric Acids, RFNA, WFNA	Nitrogen, Liquid	Nitrogen Tetroxide and MON	OTTO Fuel II	Oxygen Difluoride	Oxygen, Liquid	Pressurizing Gases	Nitromethane and Tetranitromethane
The Alcohols, CH_3OH, C_2H_5OH, $(CH_3)_2$-CHOH	●	●	●					●	●	●	●		●								
Anhydrous Ammonia, NH_3	●	●	●					●	●	●	●		●								
Aniline, $C_6H_5NH_2$	●	●	●					●	●	●	●		●								
The Boranes, B_2H_6, B_5H_9				●	●																
Ethylene Oxide, C_2H_4O				●	●																
Fluorine and Fluorine-Oxygen Mixtures						●	●					●		●		●		●	●		
The Halogen Fluorides, ClF_3, ClO_3F, ClF_5, BrF_5						●	●					●		●		●		●	●		
Hydrazine and Monomethylhydrazine, N_2H_4, CH_3NHNH_3	●	●	●					●	●	●	●		●								
UDMH and Mixed Amine Fuels, $(CH_3)_2$ NNH_2	●	●	●					●	●	●	●		●								
Hydrocarbon Fuels, JP-4, JP-5, RP-1	●	●	●					●	●	●	●		●								
Hydrogen, Liquid, LH_2	●	●	●					●	●	●	●		●								
Hydrogen Peroxide, H_2O_2, greater than 52 percent						●	●					●		●		●		●	●		
Methane, Liquid or Gas, CH_4	●	●	●					●	●	●	●		●								
Nitric Acids, RFNA, WFNA, HNO_3						●	●					●		●		●		●	●		
Nitrogen, Liquid, LN_2															●					●	
Nitrogen Tetroxide and Mixed Oxides of Nitrogen, N_2O_4, MON						●	●					●		●		●		●	●		
OTTO Fuel II																	●				
Oxygen Difluoride, OF_2						●	●					●		●		●		●	●		
Oxygen, Liquid, LO_2						●	●					●		●		●		●	●		
Pressurizing Gases															●					●	
Nitromethane and Tetranitromethane, CH_3NO_2, $C(NO_2)_4$																					●

NOTE: The bullet ● at an intersection of horizontal and vertical columns shows those propellants which may be stored together.

TABLE 4.11

B_2H_6 PROPELLANT VALVE DESCRIPTION (REF. 4.24)

Manufacturer	Annin
Model	1620
Size	1 Inch
Temperature	Ambient to -320 F
Rating	1440-psig Maximum Inlet
Service	Liquid and/or Gaseous B_2H_6
Body Material	300 Series Stainless Steel
Body Type	Globe
Connections	1-Inch and 10050 Female
Packing	Teflon
Bonnet	Standard Normalizing Finned
Stem Material	300 Series Stainless Steel
Plug Material	300 Series Stainless Steel
CV and Form	12.0 Semithrottle
Seat Material	Teflon
Flow Direction	Over Plug
Actuator Type	12.5-in.^{2} Cylinder
Action	Air-to-Open
Gaskets Material	Aluminum
Accessories	1/4-Inch, 4-Way, Explosive-Proof Solenoid Valve, 115-vac Exhar Two-Position Limit Switches, Hermetically Sealed

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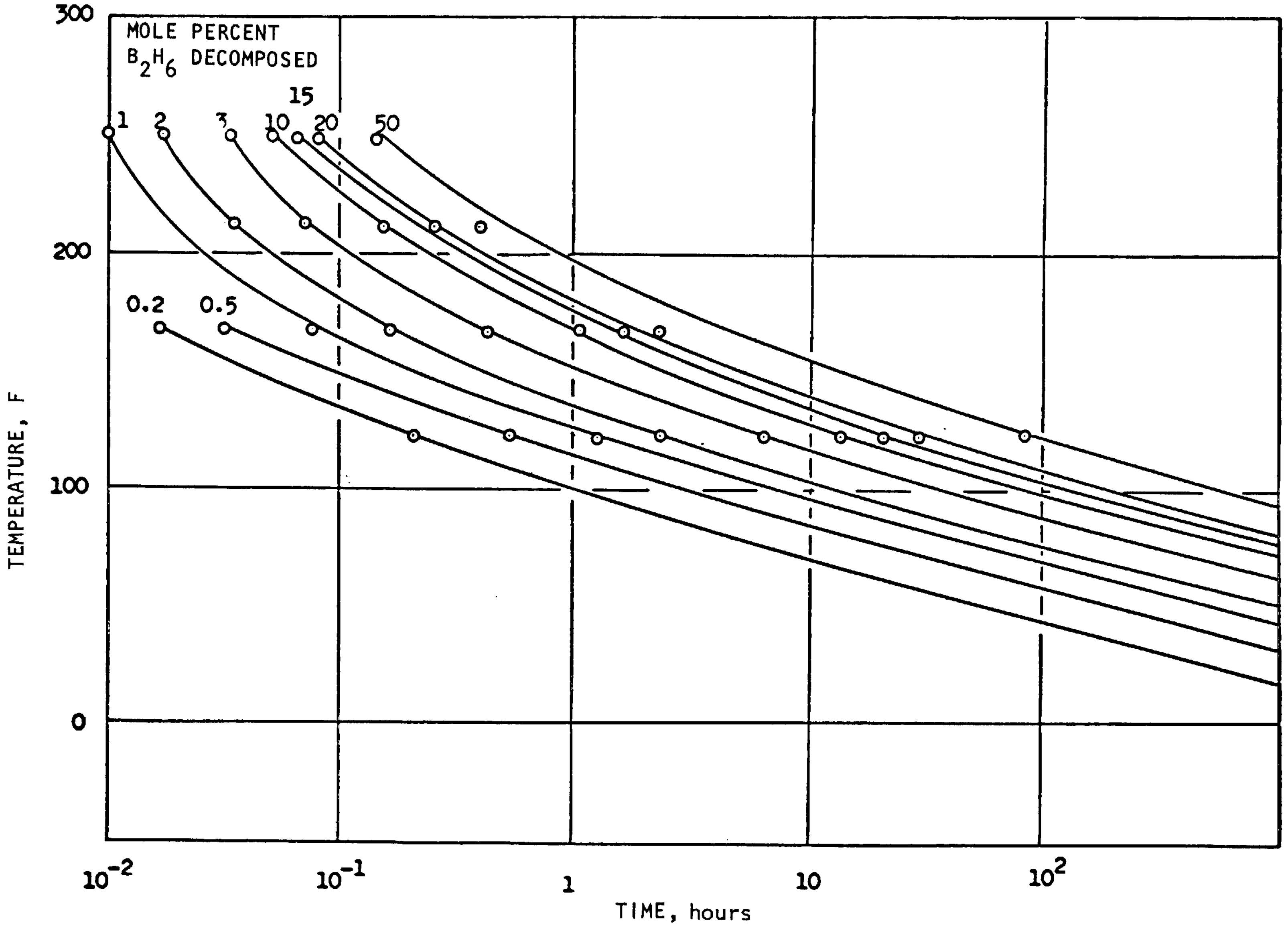

Figure 4.1. Diborane Decomposition (Reprinted from Ref. 4.4)

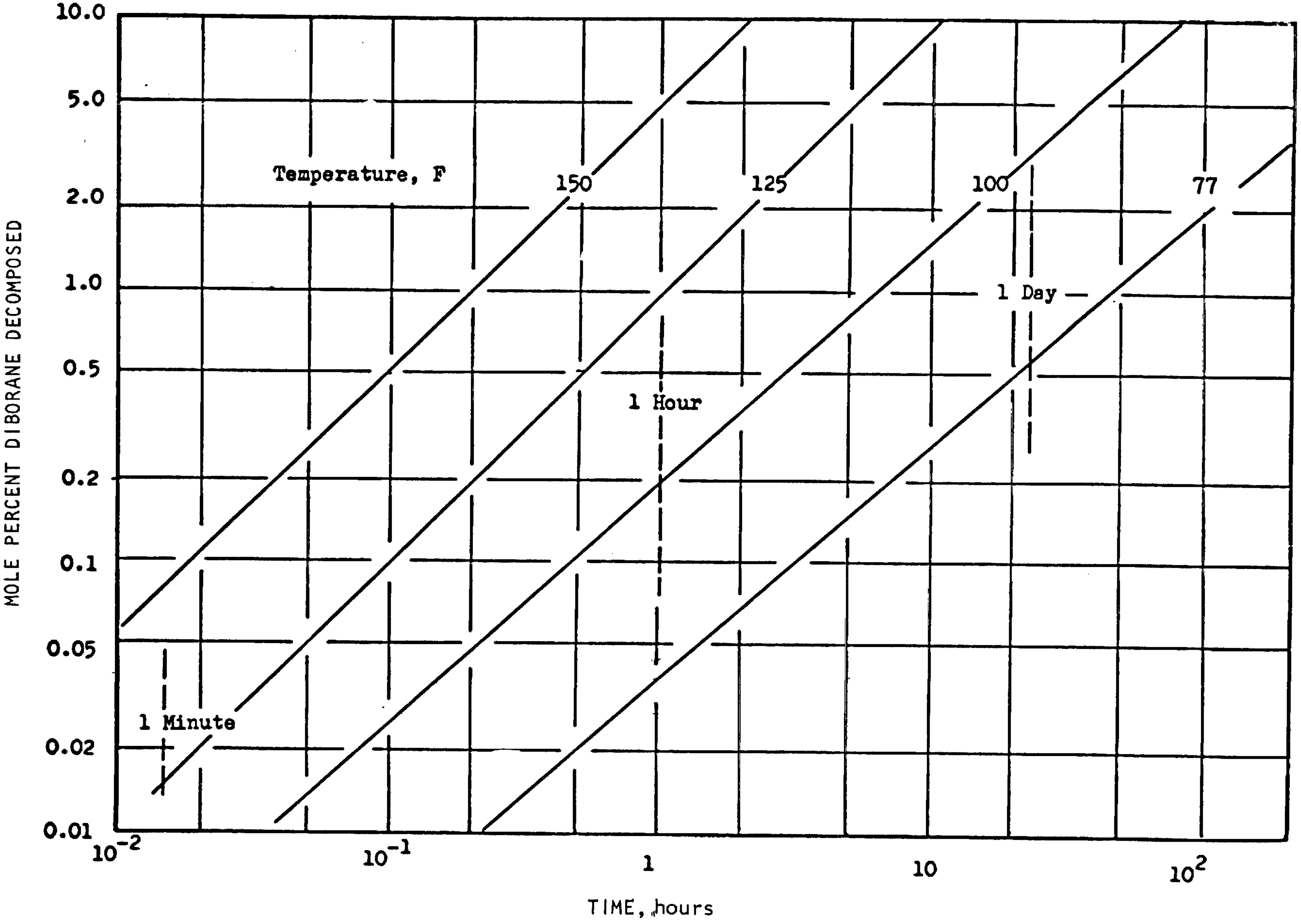

Figure 4.2. Extrapolation of B_2H_6 Decomposition Data (Reprinted From Ref. 4.4)

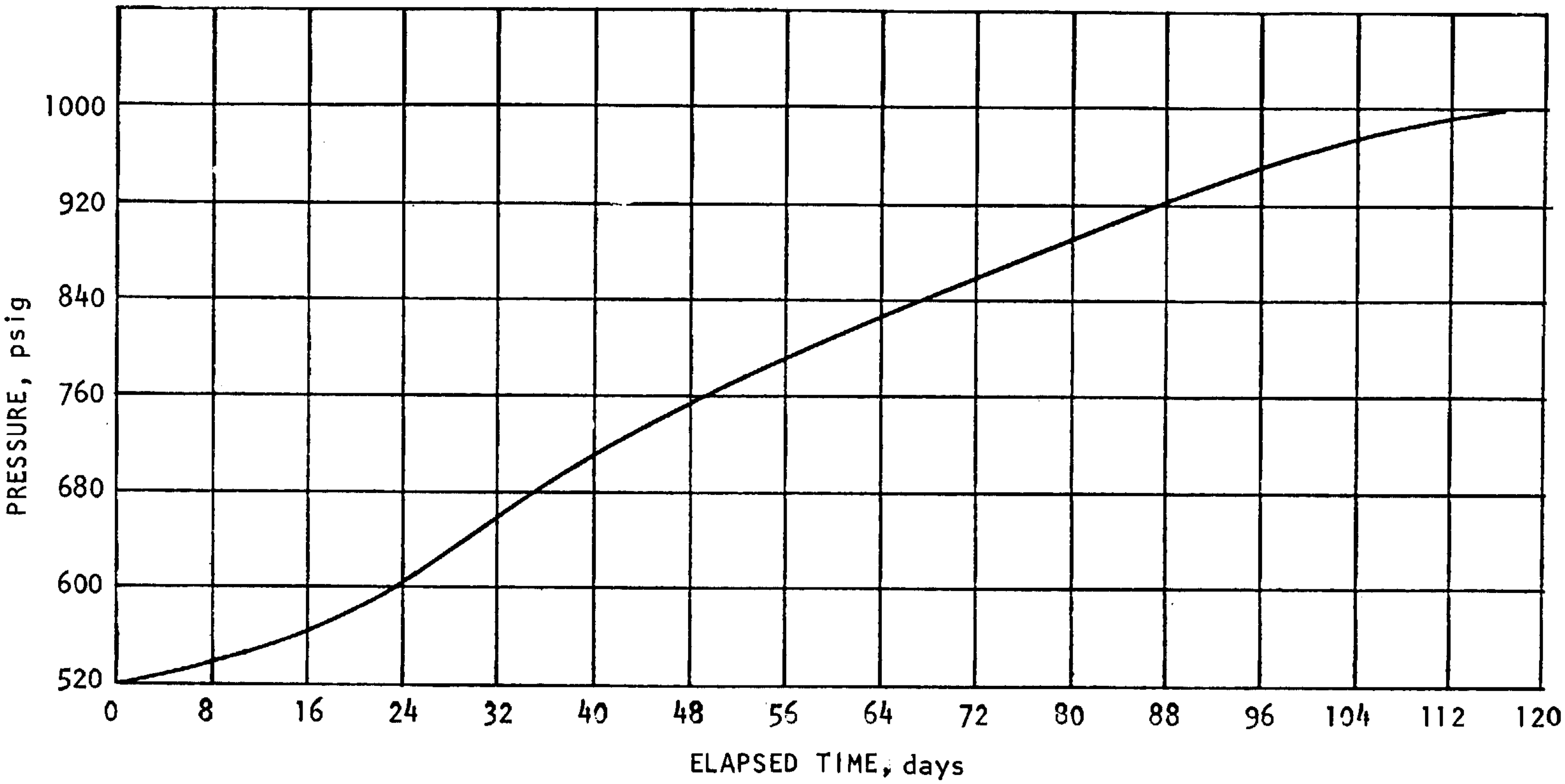

Figure 4.3. Results From B_2H_6 (Gas) Storage Tests in Stainless Steel at 25 C (77 F) (Reprinted from Ref. 4.6)

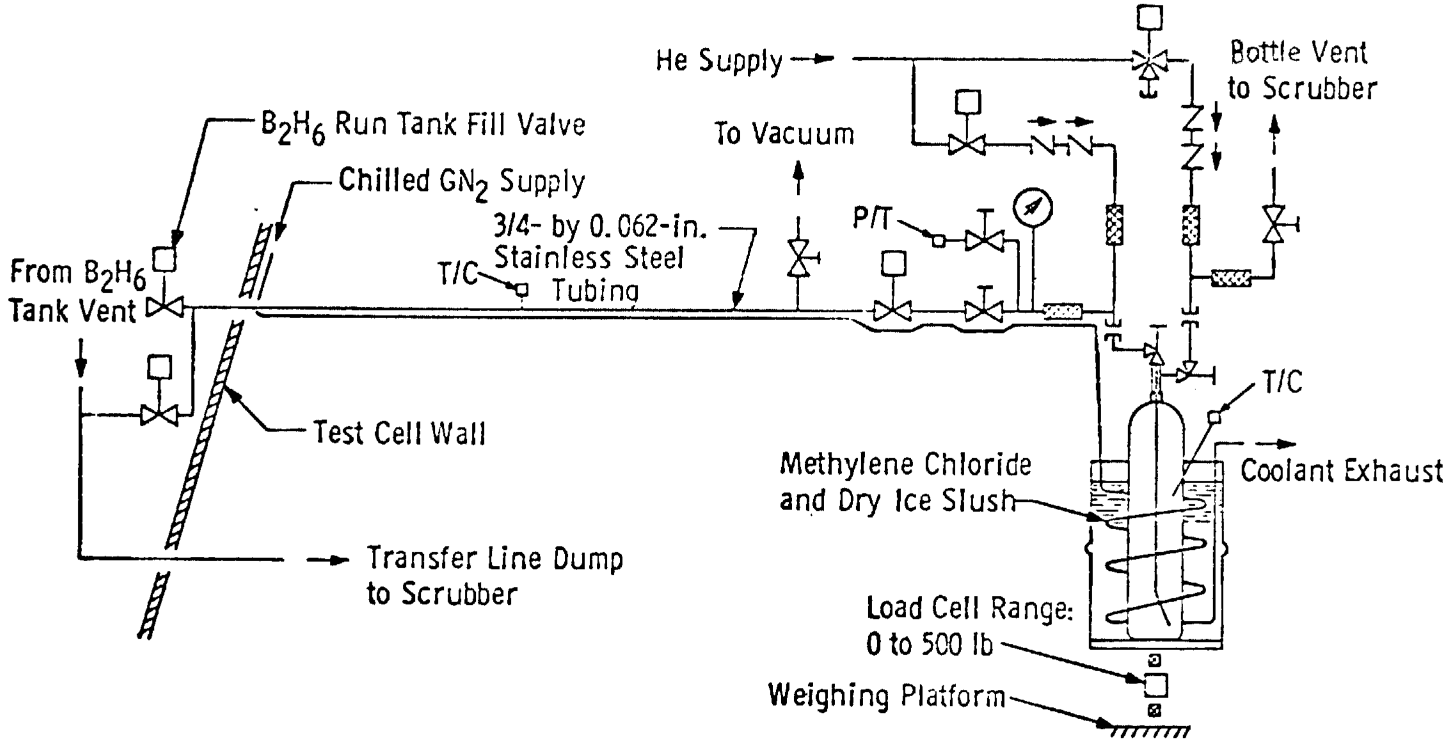

Figure 4.4. B_2H_6 Transfer System Schematic (Ref. 4.24)

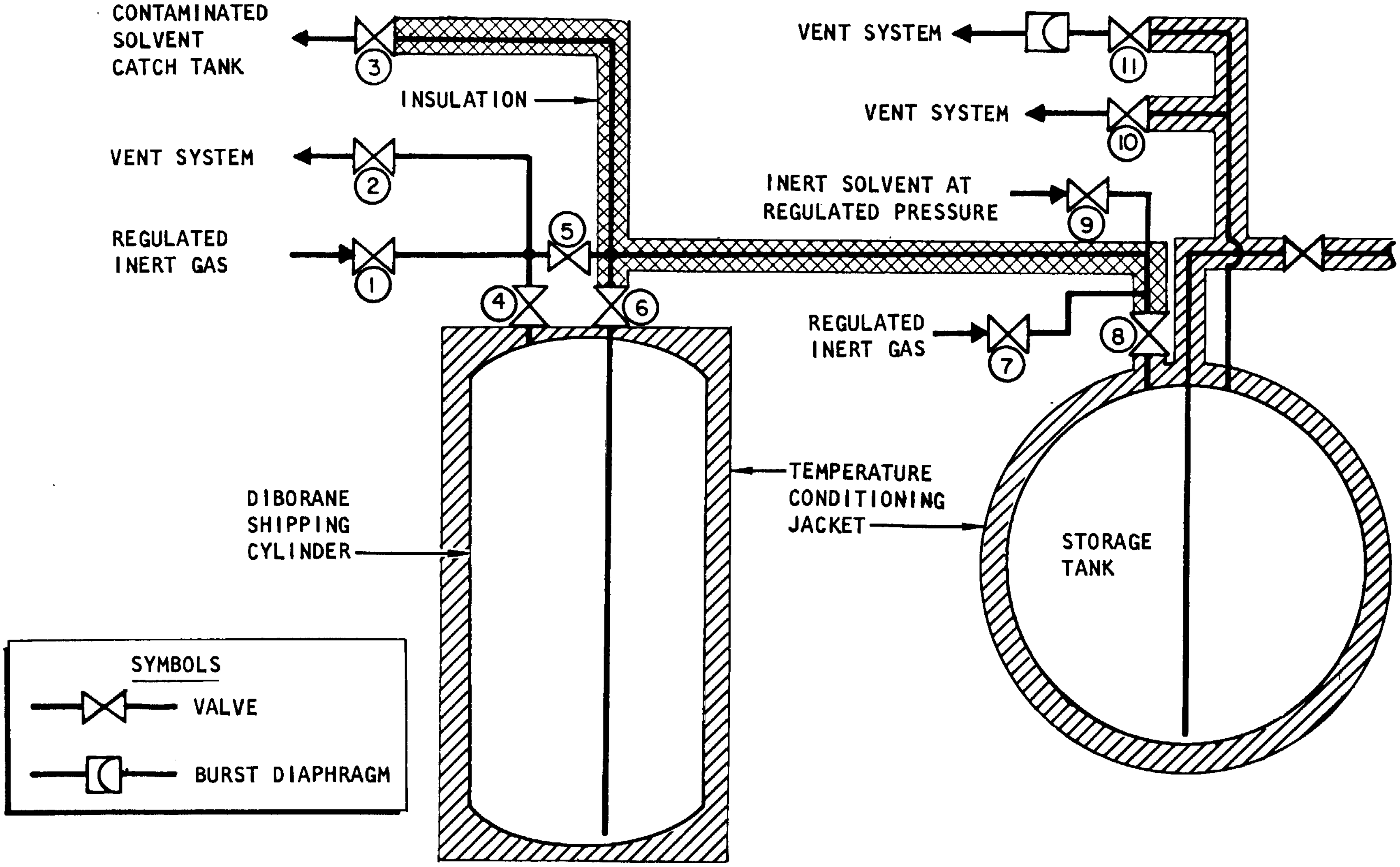

Figure 4.5. Simplified System Schematic for Transfer of B_2H_6 From Shipping Cylinder to a Storage Tank

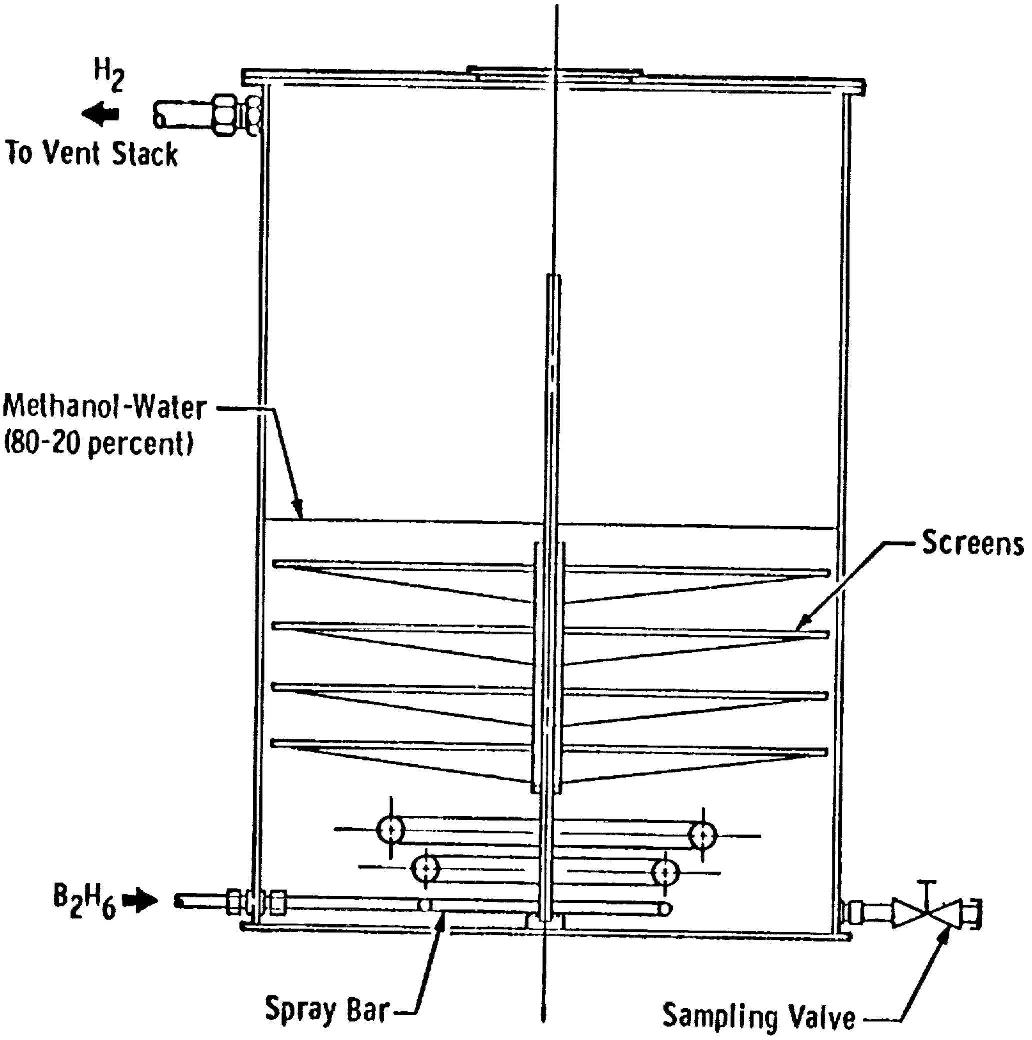

Figure 4.6. B_2H_6 Scrubber Detail (Ref. 4.24)

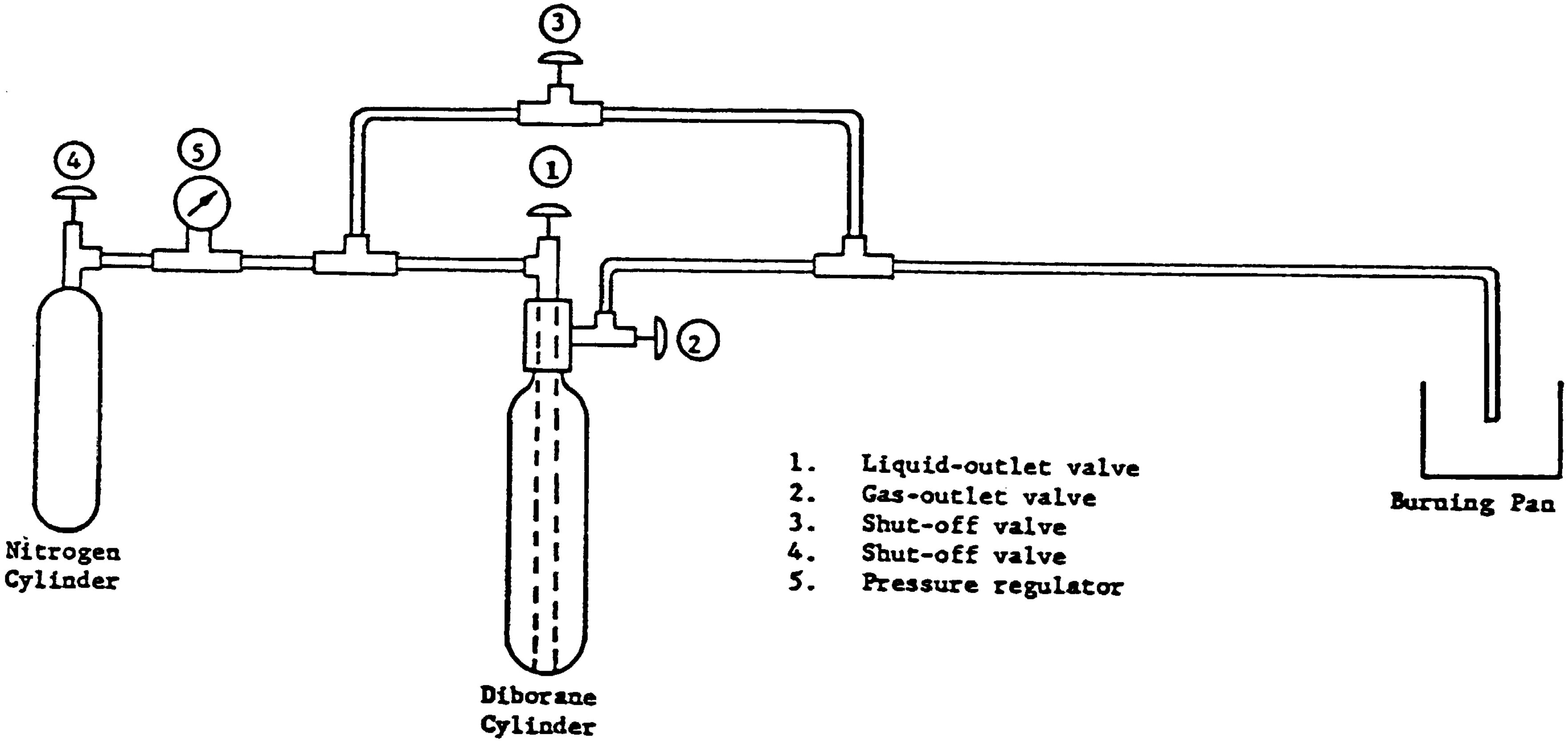

Figure 4.7. Diborane Disposal System (Ref. 4.1)

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SECTION 5: TRANSPORTATION

At the present, shipment of B_2H_6 is authorized by the Department of Transportation only under the conditions of a special permit. All shipments must be made in DOT-approved containers (Section 5.1) and packaged according to the appropriate regulations (Section 5.2). The information contained in this section is intended only as a guide to the user, and more detailed and/or current information should be acquired from the Department of Transportation and the commercial manufacturer.

5.1 SHIPPING CONTAINERS AND VEHICLES

Currently, B_2H_6 is shipped as a compressed gas in 100-gram lots, or as a liquid in two different sized cylinders (of 1 to 4 pounds or $\leq$ 40-pound capacities, respectively) packaged in drums or wooden crates with dry ice. A shipping cylinder, containing up to 200 pounds, is being designed by the manufacturer of B_2H_6 to meet near future requirements for the larger quantities. In addition, the development of a new multipurpose mobile B_2H_6 Dewar of 800-pounds capacity has been proposed to meet potential logistics support requirements for the launch of a propulsion module containing B_2H_6 at Kennedy Space Center/Air Force Eastern Test Range. These current and proposed shipping containers are described in the following paragraphs.

5.1.1 Current Shipping Containers of 100-Gram, 1 to 4-Pound, and $\leq$ 40-Pound Capacities

The specifications for currently available B_2H_6 shipping containers of 100-gram, 1 to 4-pound, and 40-pound capacities are described in Ref. 5.1 (Ref. 5.2). "Diborane is shipped in standard ICC 3AA series cylinders. Two valves with 0.903-inch right-hand threaded male outlets (protected by threaded brass caps) are mounted on a threaded tee on the head of the cylinder. The liquid-outlet valve, mounted vertically, is attached to a brass dip tube that extends to within 1/2 inch of the bottom of the cylinder. The gas-outlet valve is mounted horizontally and is used either for introduction of an inert gas into the cylinder to force liquid B_2H_6 out through the liquid-outlet valve or for release of B_2H_6 as a gas." (Ref. 5.1)

The design specifications for each of the cylinders in present use are as follows:

Specifications			
Cylinder Volume (maximum), cu in.	231	913	3985
Propellant Capacity (Net Weight)	100 g (gas)	1 to 4 pounds (liquid)	≤ 40 pounds (liquid)
Tare Weight, pounds	15	35	195
Service Pressure, psig	1800	2015	2400
Gas-Outlet Valve	Horizontally mounted, brass, Superior, with frangible disc; outlet is CGA-541 0.903-inch, 14 NGO R.H., with brass cap.		
Liquid-Outlet Valve	Vertically mounted, brass, Superior, with frangible disc; outlet is CGA-541 0.903-inch, 14 NGO R.H., with brass cap; 1/4-inch brass dip tube extends nearly to bottom of cylinder.		

The 231-cu in. cylinder containing ≤100-grams B_2H_6 gas is packaged and shipped inside a wooden crate. The 913-cu in. cylinder containing 1 to 4 pounds of liquid B_2H_6 is packaged and shipped inside a 55-gallon, insulated steel drum packed with dry ice, as illustrated in Fig. 5.1. The 3985-cu in. (≤ 40 pounds) liquid container is packed and shipped in an insulated wooden crate packed with dry ice. These outer containers are sufficiently packed therein with dry ice to provide refrigeration for a period of at least 14 days. When these drum and/or wooden crate outer containers are kept filled with dry ice, the liquid B_2H_6 shipping cylinders may serve as convenient storage containers.

5.1.2 200-Pound Capacity Shipping Container (In Design)

A skid-mounted, dry-iced shipping container with a liquid B_2H_6 capacity of 200 pounds is presently being developed by the Callery Chemical Company under Contract NASw-1827 (Ref. 5.3). The design of this container, illustrated in preliminary form in Fig. 5.2 and 5.2a, will not be finalized until the end of June 1970 (Ref. 5.2). After the design of the 200-pound liquid container is approved by the Department of Transportation, the containers will be fabricated. These containers are expected to be in service by January 1971 (Ref. 5.2).

5.1.3 800-Pound Mobile Transport Unit (Proposed)

In performance of a program under Contract NAS7-742 to study prelaunch mission operations for a space-storable propulsion module, General Dynamics-Convair Division has proposed (Ref. 5.4) the development of a road transport unit with an 800-pound (32-cu ft) liquid B_2H_6 capacity. This mobile multipurpose B_2H_6 dewar would be used as a transport unit from the B_2H_6 production site to the launch (or test) facilities and also as a storage unit, eliminating the need for a permanent stationary storage facility. This unit would simplify many of the logistic operations and provide safety advantages over the present shipping containers (Ref. 5.4). The suggested design for this liquid B_2H_6 mobile transport unit is briefly illustrated in Fig. 5.3. The design features of this unit, described in detail in Ref. 5.4, are as follows.

"Basically, the dewar consists of two refrigerant tanks enclosed in an outer vacuum shell insulated with 80-mesh evacuated perlite. The primary refrigerant tank holds liquid nitrogen, held at 165 R by 45 psig back-pressure relief valves. The secondary refrigerant tank holds tetrafluoromethane, CF_4 (Freon 14), as a thermal shield around the inner diborane tank, at any desired storage temperature from solid B_2H_6 at 165 R up to liquid at 280 R." (Ref. 5.4) The dewar is designed for a hold time of >30 days without resupply of LN_2.

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"In operation, a pressure controller compares the Freon 14 tank ullage pressure with the desired set point pressure (temperature), and opens or closes the LN_2 supply valve to the refrigerating coil in the Freon tank as required to maintain the set vapor pressure. The set point dial is calibrated in temperature units rather than pressure. At 250 R, the saturation temperature change is 3° per one pound vapor pressure change, allowing a probable temperature control accuracy of ±3 R." (Ref. 5.4)

"Liquid nitrogen at 165 R is above the freezing point of Freon 14, allowing the Freon 14 to act as a passive liquid heat transfer media and thermal shield around the diborane tank. Liquid nitrogen flow is by gravity only for simplicity. A pump can be added to reduce line sizes. Heat of vaporization is absorbed in the Freon tank at about 100° ΔT, the gaseous nitrogen then superheating to 250 R as it passes to the ullage coil and vents back to the nitrogen tank vent line." (Ref. 5.4)

"Design of the dewar is dictated primarily by safety considerations to assure a controlled, loss-free storage of diborane regardless of system or component malfunction. Failure analysis indicates fail-safe operation, as follows:

1) If electrical or pneumatic power fails: LN_2 supply valves go open. Action option:
    a) Allow Freon to chill to 165 R, freezing the diborane.
    b) Use manual LN_2 supply valve to maintain proper temperature.
2) LN_2 supply valve sticks open: same as electrical power failure.
3) LN_2 supply valves (both) stick closed: open manual by-pass to control set temperature, or to freeze the diborane.

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4) Pressure transducer/controller system signals low temperature, closing LN_2 valve: Use manual by-pass control.

5) All LN_2 valves stick closed, Freon 14 high pressure alarm also fails, LN_2 line ruptures, or no one is present to take action: Freon 14 rises in pressure and in temperature to 280 R and is maintained there by boiloff relief valves set at 15 psig. Hold time without resupply of Freon: 30 days.

6) Freon relief valves both fail to open: rupture disk bursts, venting off inert Freon 14 gas, dropping Freon pressure to atmospheric and temperatures to 260 R. 30 day hold time without resupply of Freon.

7) LN_2 relief valves fail open, or fail closed and the rupture disk bursts: LN_2 pressure drops to atmospheric and temperature drops to 140 R. Temperature control continues normally, but localized solidification of Freon may occur. If LN_2 refrigerating coil is flooded, Freon 14 as well as diborane will solidify." (Ref. 5.4)

5.2 MARKING AND PACKAGING REGULATIONS

Diborane is classified by the DOT as a "Flammable Compressed Gas", Red Label. In addition to the Red Label, all B_2H_6 shipping containers must be marked and packaged in accordance with DOT Special Permit 970 (Ref. 5.5) for refrigerated shipments and DOT Special Permit 930 (Ref. 5.6) for nonrefrigerated shipments.

Under SP 970, each outside shipping container shall also bear a conspicuous label reading as follows: "IF NOT DELIVERED BEFORE__________, CARRIER MUST ADVISE [Shipper], ALSO THE BUREAU OF EXPLOSIVES, NEW YORK, NEW YORK, BY WIRE." The date inserted in the blank space shall not exceed the number of days in shipment prescribed for each type of

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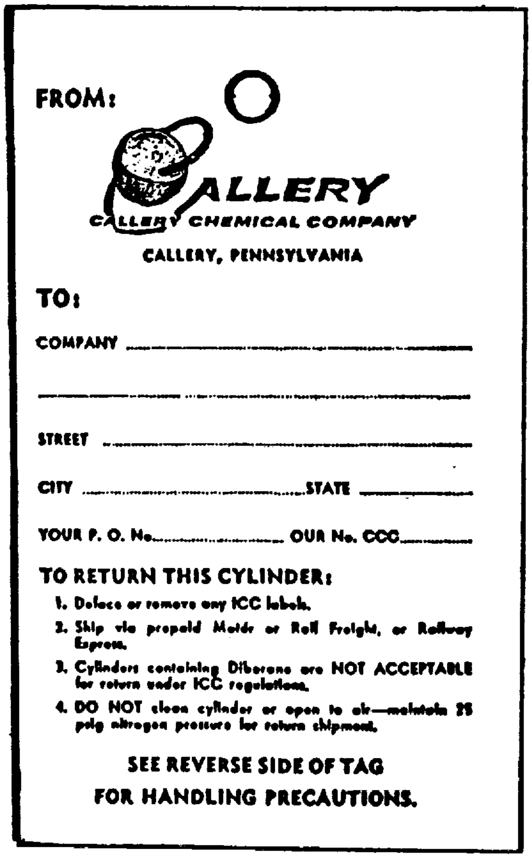
packaging (Ref. 5.5). In addition, each bill of lading, shipping order, or other shipping paper issued in lieu thereof, following the description of the commodity shall show the following notation:

> "D.O.T. SPECIAL PERMIT NO. 970. DATE OF
> SHIPMENT__________. IF NOT DELIVERED
> BEFORE_______DAYS, CARRIER MUST ADVISE
> BUREAU OF EXPLOSIVES, NEW YORK, NEW YORK,
> BY WIRE."

If the B_2H_6 is to be shipped under SP 930, all shipping orders, bills of lading, or other shipping papers must contain the notation, "DOT SPECIAL PERMIT NO. 930", following the description of the commodity and the label notation. In addition, each outside package or each cylinder authorized for shipping without the necessity of outside packaging shall be marked "DOT SP 930" (Ref. 5.6).

In addition to the labels prescribed by the Department of Transportation, the B_2H_6 cylinders have a tag wired to the cylinder containing the following information (Ref. 5.1 and 5.2):



FROM:

CALLERY
CALLERY CHEMICAL COMPANY
CALLERY, PENNSYLVANIA

TO:

COMPANY ____________________

____

STREET ____________________

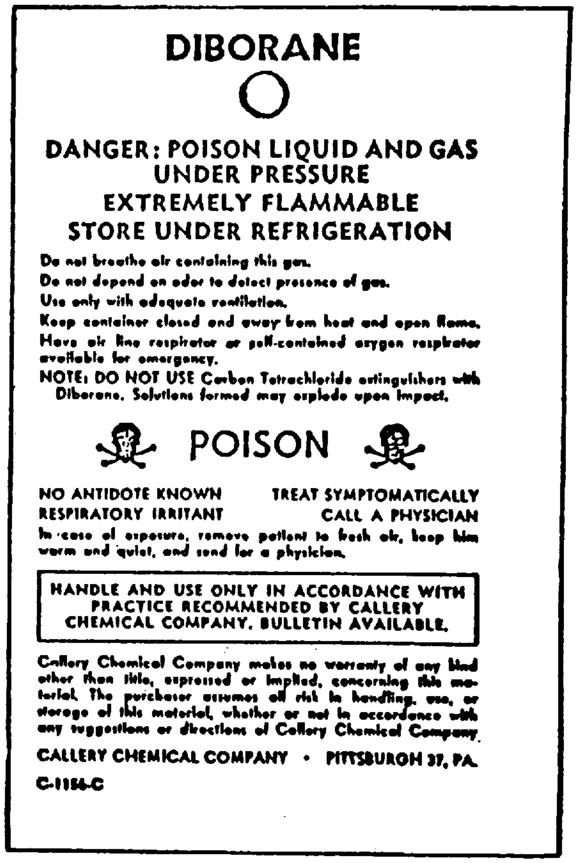
CITY ____________________ STATE __________

YOUR P. O. No.__________ OUR No. CCC__________

TO RETURN THIS CYLINDER:

1. Deface or remove any ICC labels.
2. Ship via prepaid Motor or Rail Freight, or Railway Express.
3. Cylinders containing Diborane are NOT ACCEPTABLE for return under ICC regulations.
4. DO NOT clean cylinder or open to air—maintain 25 psig nitrogen pressure for return shipment.

SEE REVERSE SIDE OF TAG
FOR HANDLING PRECAUTIONS.



DIBORANE

DANGER: POISON LIQUID AND GAS
UNDER PRESSURE
EXTREMELY FLAMMABLE
STORE UNDER REFRIGERATION

Do not breathe air containing this gas.
Do not depend on odor to detect presence of gas.
Use only with adequate ventilation.
Keep container closed and away from heat and open flame.
Have air line respirator or self-contained oxygen respirator available for emergency.
NOTE: DO NOT USE Carbon Tetrachloride extinguishers with Diborane. Solutions formed may explode upon impact.

POISON

NO ANTIDOTE KNOWN — TREAT SYMPTOMATICALLY
RESPIRATORY IRRITANT — CALL A PHYSICIAN

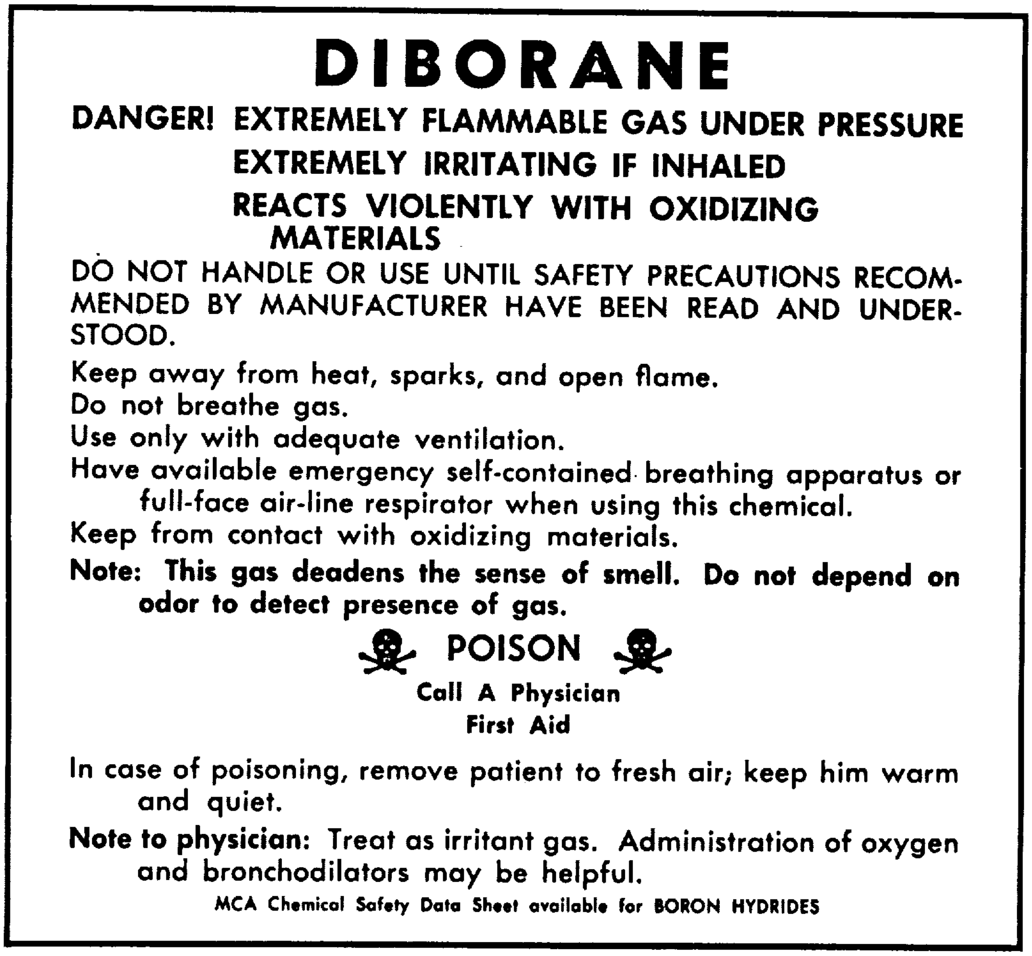
In case of exposure, remove patient to fresh air, keep him warm and quiet, and send for a physician.

HANDLE AND USE ONLY IN ACCORDANCE WITH PRACTICE RECOMMENDED BY CALLERY CHEMICAL COMPANY. BULLETIN AVAILABLE.

Callery Chemical Company makes no warranty of any kind other than title, expressed or implied, concerning this material. The purchaser assumes all risk in handling, use, or storage of this material, whether or not in accordance with any suggestions or directions of Callery Chemical Company.

CALLERY CHEMICAL COMPANY • PITTSBURGH 37, PA.
C-1156-C

The Manufacturing Chemists' Association has recommended (Ref. 5.7) use of the following label to describe the hazards which should be considered in the shipping or handling of B_2H_6:



DIBORANE

DANGER! EXTREMELY FLAMMABLE GAS UNDER PRESSURE
EXTREMELY IRRITATING IF INHALED
REACTS VIOLENTLY WITH OXIDIZING MATERIALS

DO NOT HANDLE OR USE UNTIL SAFETY PRECAUTIONS RECOMMENDED BY MANUFACTURER HAVE BEEN READ AND UNDERSTOOD.

Keep away from heat, sparks, and open flame.
Do not breathe gas.
Use only with adequate ventilation.
Have available emergency self-contained breathing apparatus or full-face air-line respirator when using this chemical.
Keep from contact with oxidizing materials.
Note: This gas deadens the sense of smell. Do not depend on odor to detect presence of gas.

☠ POISON ☠

Call A Physician
First Aid

In case of poisoning, remove patient to fresh air; keep him warm and quiet.
Note to physician: Treat as irritant gas. Administration of oxygen and bronchodilators may be helpful.

MCA Chemical Safety Data Sheet available for BORON HYDRIDES

This label, which contains information similar to that contained on the present manufacturer's tag, has a format consistent with that recommended or used on labels for all other hazardous chemicals.

5.3 SHIPPING REGULATIONS

5.3.1 Ground Transportation

All B_2H_6 shipments by ground transportation must be in accordance with DOT regulations and may be shipped only under DOT "Special Permit" (Ref. 5.5 and 5.6). Shipments are made in DOT-approved containers (Section 5.1) and packaged according to the appropriate governing regulations (Section 5.2). Shipments may be transported by rail express, private carrier, company-owned and operated motor vehicles, or by highway motor carriers that have been specifically approved for this service by the Bureau of Motor Carrier, Safety, Federal Highway Administration, Washington, D.C. (Ref. 5.5). Because shipments made under SP 970 are restricted to a certain number of days in transit (either 5 or 10 days depending on the cylinder filling density), shipments are timed so that the last day is neither a holiday nor a week-end and must be routed directly to the destination with no lay-over enroute. A shipping notice is wired on the day of shipment so that the necessary preparations can be made to receive and store the B_2H_6 promptly upon arrival at its destination (Ref. 5.1). In addition, as a further requirement of SP 970, the shipper must have an acknowledgment of receipt of the shipment by wire, to be confirmed in writing. Also, the shipper must promptly notify the Bureau of Explosives of the Association of American Railroads of any shipment that did not reach its destination within 2 days after shipment is due.

5.3.2 Commercial Air

Transportation of B_2H_6 is prohibited on passenger or cargo aircraft (Ref. 5.8 and 5.9).

5.3.3 Military Air

Diborane may not be shipped by military aircraft (Ref. 5.10).

5.3.4 Waterways

"Refer to DOT Regulations and Coast Guard Regulation CG-108 for packaging and handling information." (Ref. 5.11).

5.4 OPERATION AND MAINTENANCE OF EQUIPMENT

5.4.1 Container Handling

Users of B_2H_6 should be equipped to move the loaded and empty shipping containers in a safe manner. Recommended equipment for container handling should include fork-lift trucks or cranes equipped with lifting hooks for the larger cylinders and "bottle dollies" for the smaller cylinder. The shipping containers should not be rolled, skidded, or dropped.

Upon receival of the shipping containers, the containers should be immediately checked for leaks with a suitable borane detector (Section 6.3.1). The dry ice of the liquid shipping containers (See Section 5.1) should be checked and replenished until the B_2H_6 is emptied or transferred from the cylinders. If there is evidence of present or previous leakage, the container should be immediately transferred to a disposal area with appropriate safeguards pending further observations. If the leakage rate is sufficiently high enough to preclude further handling, the contents should be disposed of in accordance with the procedures described in Section 4.5.6. In limited leakage, the contents can be transferred into an acceptable storage container.

The shipping conainers in which the B_2H_6 is received are suitable for storage, or the B_2H_6 may be transferred to other suitable storage containers (See Section 4.4.2.1). The B_2H_6 cylinders are especially treated to insure their cleanliness and dryness and B_2H_6 can be stored for several months at -20 C (-4 F) without decomposition (See Section 4.1).

The cylinder valves should be left closed and the valve caps in place. Such storage should be in a noncombustible, well-ventilated structure in accordance with the requirements noted in Section 4.4.1.

In storage of B_2H_6 in the shipping containers, the dry ice supply surrounding the liquid cylinders must be replenished, as required. If the cylinders are removed from the outer containers and stored in an ice chest or box, care should be taken to prevent ice accumulation on the cylinders and that they are not permitted to become frozen in place. Since the cylinder material is brittle when cold, the shipping cylinders should not be stored at less than -80 C (-112 F). Precautions should be taken to ensure that cylinders stored at these low temperature levels are not bumped, dropped, or subjected to sudden pressure surges (Ref. 5.1). Periodic inspections of the tightness of the stem and the packing nut should be made to guard against leakage; occasional leak tests should be conducted with a suitable detector (See Section 6.3.1).

Because the transportation time limit is used only for the original shipment, full or partially filled cylinders cannot be returned to the manufacturer or shipped elsewhere, unless a copy of the permit is granted to the new shipper. Such shipments may be authorized under the terms of the permit. If the "empty" cylinders are returned to the manufacturer, the residual B_2H_6 remaining in the cylinders should be disposed of (See Section 4.5.6) and the cylinders prepared as follows (Ref. 5.1).

WARNING

Do not use empty diborane cylinders as temporary storage for other fuels, solvents, or other materials.

The "empty" cylinders should be flushed with nitrogen for 5 minutes to assure removal of essentially all of the B_2H_6 and then pressurized to 25 psig. The valve outlet caps must be replaced and closed securely, and the valve protective caps must be replaced before the containers are offered for the return shipment. The lower portion of the DOT combination label-shipping tag, if attached to the cylinder, must be removed. If boxed cylinders are returned in original shipping cases, the DOT label on the outside package must be removed, defaced, obliterated or covered by the prescribed white DOT "Empty" label (Ref. 5.1).

5.4.2 Safety and Handling Procedures

During any operations involving the handling or transfer of B_2H_6 containers, the safety precautions and handling procedures noted in Sections 6 and 4.5, respectively, should be observed. In general, these procedures include the following:

1. Any person involved in the handling or transfer of B_2H_6 from its container should be thoroughly familiar with the physical, chemical, and engineering characteristics of B_2H_6.
2. Two operators should be available at all times during any operation involving the handling, transfer, or storage of B_2H_6, and they should be sufficiently separated so that a mishap would not incapacitate both.
3. All personnel not directly concerned with the handling operation should evacuate the hazard area.
4. Personal safety equipment should be worn during all handling operations. (See Section 6.4.1.2)
5. Water hoses, showers, and other appropriate safety equipment should be available in the immediate vicinity of the handling area. The location and proper function of this equipment should be checked before beginning any operation.
6. Whenever possible, B_2H_6-containing systems should be remotely controlled.

5.4.3 Transfer of Propellant

Diborane can be discharged from its shipping cylinder storage container by its own vapor pressure or by pressurizing the container with dry inert gas. The inert gas pressurization method is used almost exclusively at the present time for unloading cylinders, because this technique is extremely reliable. The preferred techniques are discussed in detail in Section 4.5.3.

5.5 TRANSPORTATION ACCIDENT PROCEDURE

If a vehicle transporting diborane is involved in an accident or a container develops leaks, the following procedures are recommended:

1. If possible, the vehicle should be parked off the roadway, and flags and flares should be set out.
2. Traffic should not be allowed to approach closer than 100 yards, and unauthorized personnel should be kept upwind.
3. Local police, fire authorities, and the shipper should be notified, but the vehicle should not be left unattended.
4. Precautions should be taken to prevent personnel injury which would result from inhalation of vapors or contact with spills of the propellant. This includes informing the local police and fire authorities as to the nature and potential health hazards of B_2H_6.
5. All precautions prescribed for flammable materials (no open flames, no smoking, etc.) should be observed, although B_2H_6 will probably ignite if spilled.

6. In case of fire, the fire should be controlled with water fog. The fire should not be extinguished unless the B_2H_6 is completely consumed or the B_2H_6 source is closed to the atmosphere (See Section 6.3.3).

WARNING

DO NOT USE CARBON TETRACHLORIDE.

Halogenated hydrocarbons such as carbon tetrachloride may react violently or form impact sensitive mixtures with B_2H_6 and should never be used to fight B_2H_6 fires.

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5.6 REFERENCES

5.1 Yaffe, B. S., Diborane, Space Storable Fuel, Callery Chemical Company, Callery, Pennsylvania, January 1962.

5.2 Private Communications, A. J. Toering, Callery Chemical Company, to K. J. Youel, Rocketdyne, 6 April, 10 April, and 19 May 1970.

5.3 Callery Chemical Company, Diborane Storage and Transport, Contract NASw-1827, Callery, Pennsylvania, program in progress.

5.4 GDC-BNZ 69-013-7, A Study of Prelaunch Operations for a Space Storable Propellant Module, Final Report, Contract NAS7-742, General Dynamics, Convair Division, San Diego, California, March 1970.

5.5 Department of Transportation Special Permit 970, 28th revision, 6 February 1969, Expiration Date: 31 January 1971.

5.6 Department of Transportation Special Permit 930, 25th revision, 30 January 1969, Expiration Date: 31 January 1971.

5.7 Manufacturing Chemists Association, "Boron Hydrides," Chemical Safety Data Sheet SD-84, 1961.

5.8 "Official Air Transport Restricted Articles Tariff No. 6-D," January 1970.

5.9 International Air Transport Association, "Restricted Articles Regulations," 12th edition, 1 July 1969.

5.10 AFM 71-4, "Packaging and Handling of Dangerous Materials for Transportation by Military Aircraft," 15 November 1965.

5.11 CPIA Publication 194, Chemical Rocket/Propellant Hazards, Volume III - Liquid Propellant Handling, Storage, and Transportation, the JANNAF Hazards Working Group, JANNAF Propulsion Committee, Chemical Propulsion Information Agency, Silver Spring, Maryland, May 1970.

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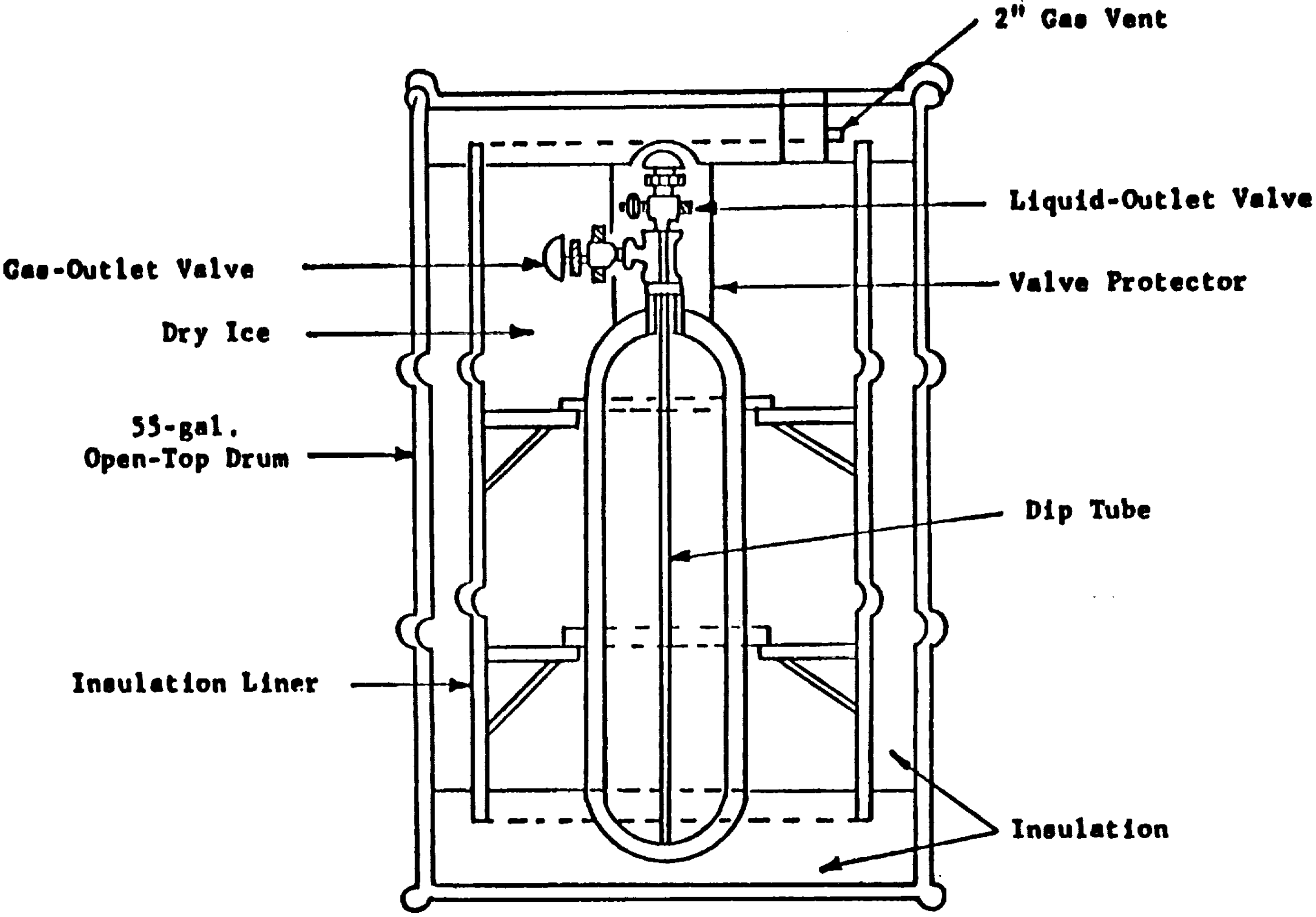

Figure 5.1. Shipping Container for Liquid Diborane of 1 to 4 Pound Quantities (Reprinted from Ref. 5.1)

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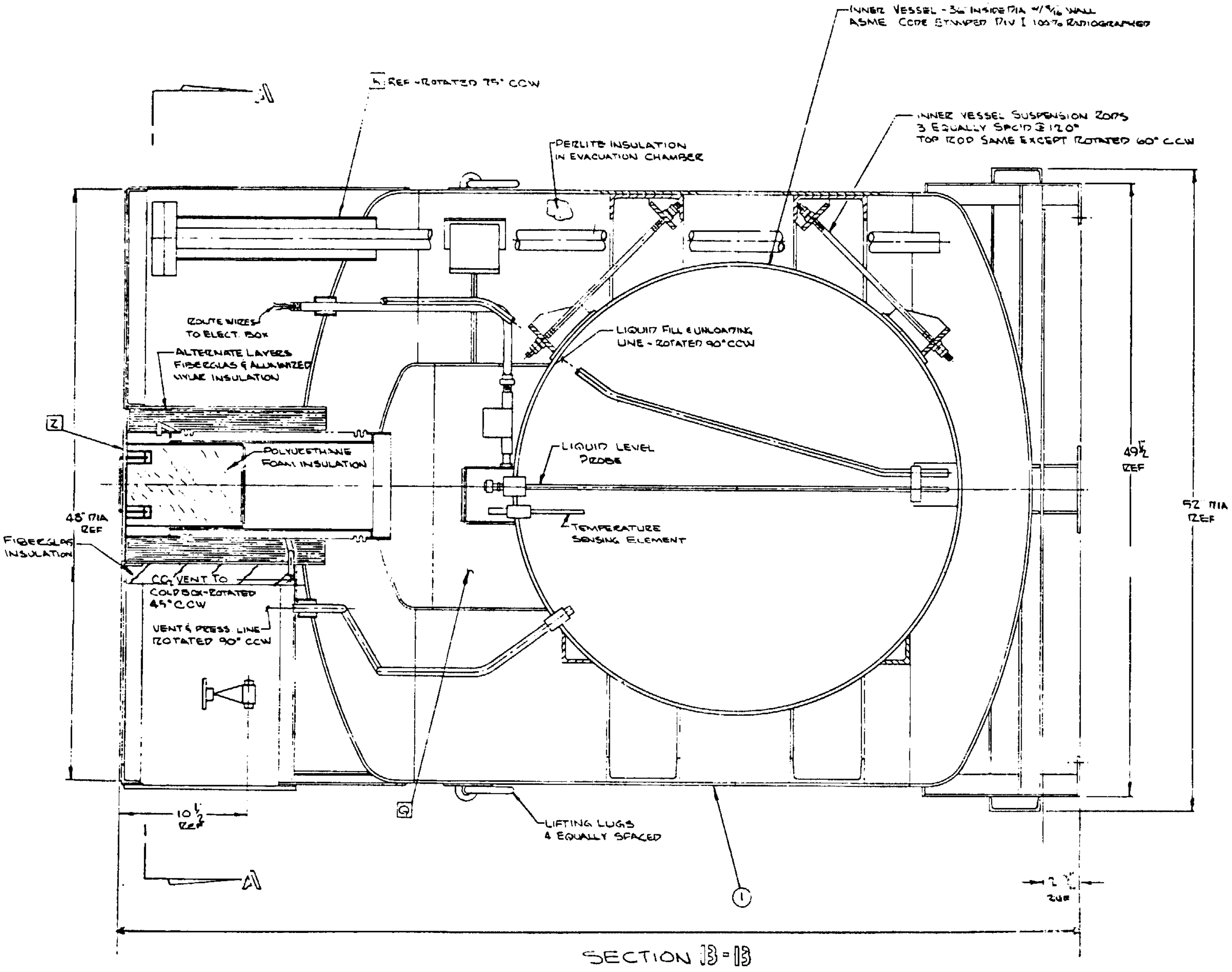
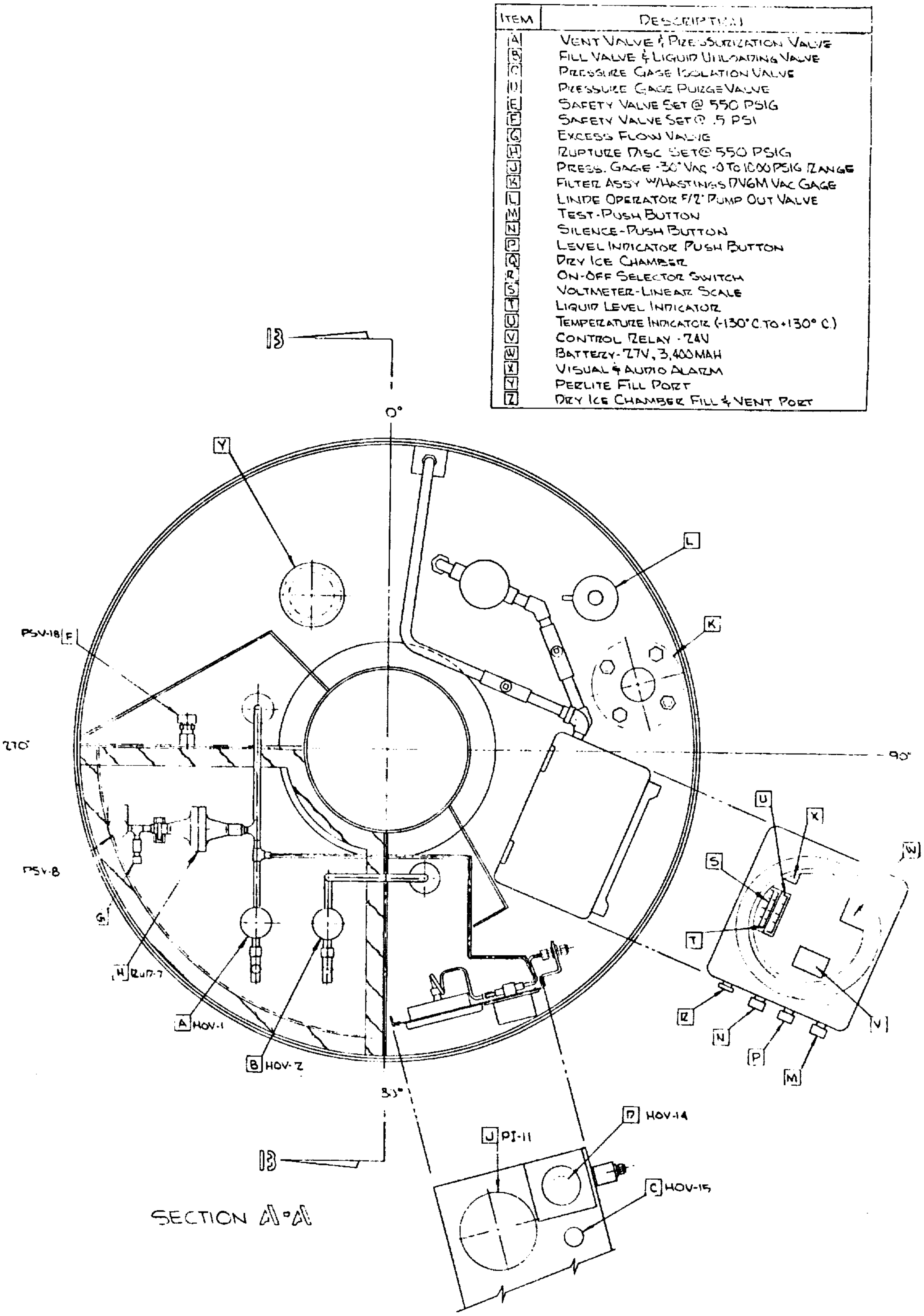
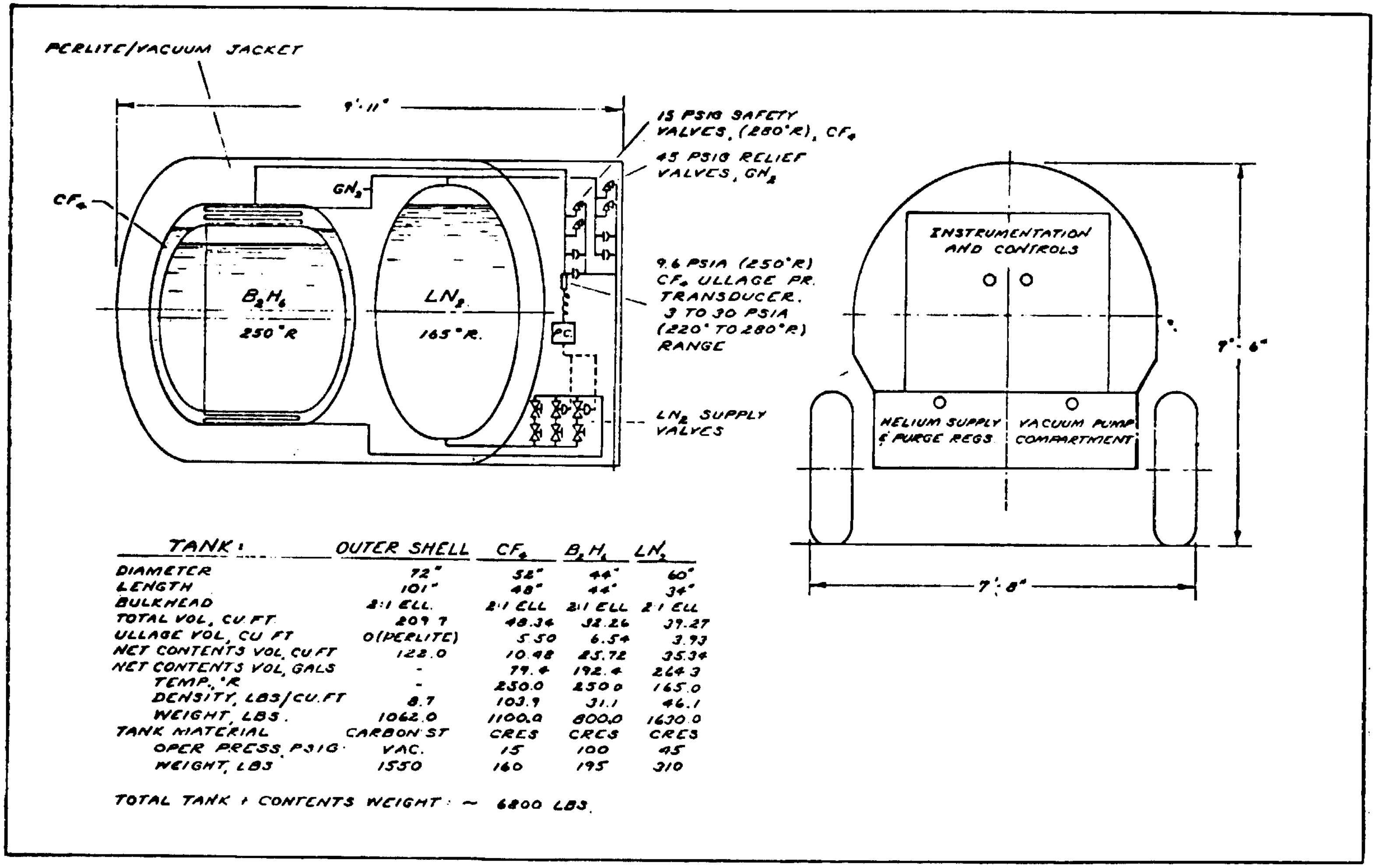


Figure 5.2. Proposed 200-Pound B_2H_6 Shipping Container, Elevation View (Ref. 5.2)



ITEM	DESCRIPTION
A	VENT VALVE & PRESSURIZATION VALVE
B	FILL VALVE & LIQUID UNLOADING VALVE
C	PRESSURE GAGE ISOLATION VALVE
D	PRESSURE GAGE PURGE VALVE
E	SAFETY VALVE SET @ 550 PSIG
F	SAFETY VALVE SET @ .5 PSI
G	EXCESS FLOW VALVE
H	RUPTURE DISC SET @ 550 PSIG
J	PRESS. GAGE -30" VAC -0 TO 1000 PSIG RANGE
K	FILTER ASSY W/HASTINGS DV6M VAC GAGE
L	LINDE OPERATOR F/2" PUMP OUT VALVE
M	TEST-PUSH BUTTON
N	SILENCE-PUSH BUTTON
P	LEVEL INDICATOR PUSH BUTTON
Q	DRY ICE CHAMBER
R	ON-OFF SELECTOR SWITCH
S	VOLTMETER-LINEAR SCALE
T	LIQUID LEVEL INDICATOR
U	TEMPERATURE INDICATOR (-130°C TO +130° C)
V	CONTROL RELAY - 24V
W	BATTERY - 27V, 3,400 MAH
X	VISUAL & AUDIO ALARM
Y	PERLITE FILL PORT
Z	DRY ICE CHAMBER FILL & VENT PORT

Figure 5.2a. Proposed 200-Pound B_2H_6 Shipping Container, Plan View (Ref. 5.2)



TANK:	OUTER SHELL	CF_4	B_2H_6	LN_2
DIAMETER	72"	52"	44"	60"
LENGTH	101"	48"	44"	34"
BULKHEAD	2:1 ELL.	2:1 ELL	2:1 ELL	2:1 ELL
TOTAL VOL, CU FT	209.7	48.34	32.26	39.27
ULLAGE VOL, CU FT	0(PERLITE)	5.50	6.54	3.93
NET CONTENTS VOL, CU FT	122.0	10.48	25.72	35.34
NET CONTENTS VOL, GALS	-	79.4	192.4	264.3
TEMP., °R	-	250.0	250.0	165.0
DENSITY, LBS/CU.FT	8.7	103.9	31.1	46.1
WEIGHT, LBS.	1062.0	1100.0	800.0	1630.0
TANK MATERIAL	CARBON ST	CRES	CRES	CRES
OPER PRESS, PSIG	VAC.	15	100	45
WEIGHT, LBS	1550	160	195	310

TOTAL TANK + CONTENTS WEIGHT: ~ 6800 LBS.

Figure 5.3. Proposed Liquid B_2H_6 Mobile Transport Dewar (Reprinted From Ref. 5.4)

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SECTION 6: SAFETY

6.1 HAZARDS

The potential hazards involved in the use of B_2H_6 are associated with three of the general health hazard categories: toxicity (physiological activity), flammability, and explosivity. Diborane is a highly toxic chemical and serious personnel health hazards can result from inhalation or ingestion of, or cutaneous exposure to, its liquid and/or vapors and many of its reaction and decomposition products. It is classified as a "Flammable Compressed Gas" (Red Label) by the Department of Transportation and will almost always ignite on contact with air. Although B_2H_6 will undergo rapid decomposition when subjected to extreme temperatures and can form explosive mixtures with air (like most fuels), it is not sensitive to mechanical shock and does not present an unusual explosion hazard. While these hazards may sound ominous, it should be noted that similar hazards exist for many chemical compounds which are in widespread use and are safely handled by industry. Thus, adequately trained personnel with full knowledge of the potential hazards and their control and following prescribed procedures can safely handle B_2H_6 in any required operation.

6.1.1 Physiological Effects

There are three main routes by which intoxicating substances can enter the body: (1) vapor inhalation through the nose or mouth, (2) cutaneous absorption of the liquid or vapor, and (3) ingestion. Intoxication from B_2H_6 occurs almost exclusively by inhalation. Cutaneous absorption and ingestion of B_2H_6 are much less likely although cutaneous absorption of B_2H_6 reaction products, decomposition products, and solutions is a distinct possibility.

6.1.1.1 Vapor Inhalation

Diborane as a toxic chemical is primarily a pulmonary irritant. Inhalation of B_2H_6 vapors produces an exothermic reaction in the lungs as the borane is rapidly hydrolyzed to boric acid and hydrogen. Although boric acid has been reported to be mildly toxic (Ref. 6.1 and 6.2), the chief danger from inhalation of B_2H_6 appears to arise from the local action of the gas on the respiratory surface (Ref. 6.3 and 6.4); small smounts of boric acid would probably be slowly eliminated through the urine. Animal studies have also indicated that severe exposure could impair the central nervous system (Ref. 6.5 and 6.6), possibly by blocking the oxidation-reduction enzymes.

Extensive animal experimentation and clinical observations with B_2H_6 and other boranes as well as limited observations of their effects on humans have been reported in Ref. 6.3, 6.4, and 6.7 through 6.20. The results of these and other investigations, although somewhat difficult to evaluate and compare, do reach the conclusion that the primary physiological hazard of B_2H_6 is to the respiratory system. Many of these experiments have been reviewed in detail in Ref. 6.2, 6.4, and 6.21.

The threshold limit value (TLV) presently used for B_2H_6 has been established by the American Conference of Governmental Industrial Hygienists as 0.1 ppm by volume. This value represents the average concentration over a normal work day to which the average human can be safely exposed on a daily basis with no adverse effects.

Occasionally, emergencies may occur in which a person would be exposed to B_2H_6 at very high concentration for a brief time. The National Research Council's Committee on Toxicology has recommended (Ref. 6.22) Emergency Exposure Limits (formerly called Emergency

Tolerance Limits) to cover these accidental, emergency situations. The Committee defines its risk criteria in the following terms:

> "The Emergency Exposure Limit for short-term exposure to an airborne contaminant is a concentration which, when inhaled for a specified single brief period, rare in the lifetime of an individual, is believed not to result in a period of disability or interfere with the performance of his assigned task. In no event shall the value so selected produce danger from flammability of combustible aerosols, or result in substantial impairment of vision or visibility, or the ability to breathe."

The phrase "rare in the lifetime of an individual" is further defined so that no person will be allowed in a position where a second emergency exposure is possible until authorized to do so by the responsible physician.

The current Committee recommendations of Emergency Exposure Limits (EEL) for B_2H_6 are as follows: 10 ppm for 10 minutes, 5 ppm for 30 minutes, and 2 ppm for 60 minutes. It is emphasized that these are intended to be used in planning operations so that an accident at any time cannot expose a worker to a dangerous concentration. They are not to be used for predictable exposures of workers or for calculating safe downwind exposure conditions. Also, no safety factor for individual variability has been included. Definite effects may occur, but it is believed that they will not incapacitate a man either mentally or physically from performing an essential task.

The odor (See Section 2.1) of B_2H_6 offers some warning, but small concentrations may be below the threshold limit for detection by the nose. Prolonged exposure to small concentrations of B_2H_6 may also temporarily impair the sense of smell, so the odor should not be relied upon as a means of detection. The median detectable concentration (MDC) of B_2H_6 for man was experimentally determined

(Ref. 6.23) as 3.7 mg/m^3 (~3.2 ppm) of B_2H_6 in air; no after-effects or desensitization of the olfactory nerves were noted in these tests from short exposures to B_2H_6 in concentrations ranging from 0.2 to 6 mg/m^3. Data from these tests illustrating the detectable concentrations of B_2H_6 as a function of the percentage of the test subjects are presented graphically in Fig. 6.1. Other investigators (Ref. 6.8, 6.10, and 6.24) have reported similar values for the MDC; however, it is suspected that these data were taken from Ref. 6.23.

Depending on the concentration inhaled, B_2H_6 can cause coughing, a sense of tightness in the chest, nausea, temporary elevated pulse, blood pressure, and temperature, fatigue, heaviness of legs, headache, and skeletal muscular tremors and spasms (Ref. 6.2, 6.4, 6.7, 6.8, 6.13, and 6.25). "The initial symptoms of B_2H_6 intoxication are drowsiness, lightheadedness, and perhaps headache and mild tremors. In severe cases, the tremors may progress to muscular spasms. Prior to the patient's own realization that he has become intoxicated, co-workers may observe a slowness to respond to questions, dullness, and body movements not unlike mild alcoholic intoxication. Beyond the initial symptoms, the patient may lose control of a particular muscular function; this may be manifested as an inability to hold the head erect or to retract the tongue" (Ref. 6.26).

Although B_2H_6 is highly toxic and hospitalization has been required for numerous cases, it should be noted that most reported exposures have caused only minor distress (Ref. 6.7), and no human fatality has yet been attributed to B_2H_6 intoxication (Ref. 6.6). This can probably be explained by the fact that the distinct odor of B_2H_6 can be easily recognized; and, at the onset of the symptoms after inhalation, the workers quickly leave the contaminated area. If, however, severe exposure occurs, it is possible that bronchial pneumonia could develop (Ref. 6.5 and 6.8) with lung damage and asthmatic diathesis. The respiratory irritation caused by B_2H_6 has been reported (Ref. 6.12) to be similar to metal fume fever.

The diagnosis of B_2H_6 poisoning is only presumptive (Ref. 6.4 and 6.9) because the symptoms are respiratory and nonspecific. Although extensive research has been carried out on the toxicology of the boranes, the specific mechanism of action is still obscure and no specific therapy exists (Ref. 6.13). When B_2H_6 poisoning is suspected or diagnosed, the main problem in therapy appears to be to combat or prevent pulmonary infection (Ref. 6.10). The most effective treatment (Ref. 6.4, 6.5, and 6.8) is the prompt administration of oxygen under positive pressure (about 4 cm of H_2O pressure has been suggested in Ref. 6.4). Additional treatment would include bed rest, antibiotics if a respiratory infection is present, and/or a barbituate for convulsions if the central nervous system is involved (See Section 6.4.2).

6.1.1.2 Cutaneous. Contact of solutions containing B_2H_6 with the skin could cause skin dermatitis from the pyrolysis products (Ref. 6.5). Skin or eye membrane contact with B_2H_6 could cause burns (Ref. 6.27), presumably, as a consequence of the heat of hydrolysis or oxidation. Although there is no evidence to suggest that B_2H_6 penetrates the skin in significant amounts (Ref. 6.7), it has been reported (as summarized in Ref. 6.21) that many of the higher boranes (e.g., pentaborane) which are pyrolysis products of B_2H_6 will penetrate the skin and cause systemic poisoning in the body. Thus, solutions containing B_2H_6 should also be treated as possible sources of intoxication. This is particularly significant in solvent-type solutions where the solvent might provide the access through the skin. If B_2H_6 or any B_2H_6-solution does contact the skin or eyes, the affected areas should be immediately and thoroughly washed (See Section 6.4.2).

6.1.1.3 Ingestion. Ingestion of B_2H_6 is an unusual and unlikely occurrence, and the consequence of such an occurrence has not been determined.

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However, in the event that B_2H_6 solutions are accidently swallowed, every effort should be made to induce vomiting, by administering large quantities of salt water or baking soda solution (See Section 6.4.2).

6.1.2 Flammability and Fire Hazards

Diborane is a highly flammable gas which will sustain combustion in air at atmospheric pressure over a B_2H_6 concentration range of ~0.9 to 98 m/o. (It should also be noted that the decomposition products, i.e., H_2 and the higher boranes, have similarly wide flammability ranges.) It burns in air (or oxygen) with a blue to green flame according to the reaction:

$$B_2H_6 + 3\ O_2 \longrightarrow B_2O_3 + 3\ H_2O$$

Although the ignition temperature of pure B_2H_6 in air has been experimentally determined (Ref. 6.28) as 145 to 150 C (293 to 302 F), depending on the surface of the experimental apparatus (e.g., platinum, glass, iron, etc.), for all practical purposes B_2H_6 is generally regarded as pyrophoric at room temperature (Ref. 6.5). This unreliable pyrophoricity characteristic is a function of the effects of B_2H_6 impurities (such as the higher boranes, which are decomposition products), effects of the surfaces contacted by B_2H_6, heat of reaction from hydrolysis with moisture in the air, etc. The ignition temperature of pure B_2H_6 in oxygen was similarly determined (Ref. 6.28) in platinum tubes as 135 C (275 F). The flash point of B_2H_6 is reported in Ref. 6.29 as -90 C (-130 F).

Studies of the flammability (and explosivity) of B_2H_6 in air and oxygen have been conducted by a number of investigators. Some of this work has been referenced in Section 2.3.3 in discussion of the B_2H_6 oxidation reaction, and a summary of much of the work is presented by Adams in Ref. 6.30. In addition, the explosive oxidation of B_2H_6 is further described in Section 6.1.3.

Flammability limits of B_2H_6 in air and oxygen have been studied by Price (Ref. 6.31), Eads and Thomas (Ref. 6.32), and Olson and Setze (Ref. 6.33). The flammability limits of B_2H_6 in carbon dioxide-free air, as determined (Ref. 6.32) in a vertical glass tube with an ID of 5 cm, are presented as a function of pressure (to 1000-mm Hg) in Fig. 6.2. Diborane concentrations ranging from ~0.7 to 98 m/o were found to be flammable with a lower limit of 3 mm Hg and 15 m/o B_2H_6. At atmospheric pressure and room temperature, it was found (Ref. 6.31) that a 95 v/o B_2H_6 - 5 v/o O_2 mixture will inflame upon sparking, and that 1 to 2 v/o B_2H_6 concentration in dry air, or air-nitrogen mixtures, will yield self-sustaining flames (as shown in Fig. 6.3). Studies reported in Ref. 6.33 indicate that at 1-atmosphere pressure the lean limit for B_2H_6 occurs at an equivalence ratio (B_2H_6 concentration of the mixture/B_2H_6 concentration at stoichiometric) of ~ 0.1, which is about the same as that of hydrogen, while the rich limit occurs at an equivalence ratio of ~ 60, which is ~ 8 times richer than hydrogen.

Price (Ref. 6.34) reported peak flame speeds of up to 100 m/sec (328.1 ft/sec), in a B_2H_6-air mixture (containing ~ 8 v/o B_2H_6) flowing in a 2.5-cm tube at room temperature and atmospheric pressure (Fig. 6.4); however, the mixture frequently detonated after burning about a meter. With oxygen, mixtures containing more than 10 v/o B_2H_6 invariably detonated (See Section 6.1.3). In diborane-air flame speed studies by Parker and Wolfhard (Ref. 6.35) in a 0.4-mm tube at atmospheric pressure and room temperatures, a peak flame speed of 515 cm/sec (16.9 ft/sec) was obtained at an equivalence ratio of 1.07. These results (Ref. 6.35) were compared to those obtained from hydrogen-air flame speed studies in Ref. 6.33 (See Fig. 6.5) and indicate that the peak flame speed for B_2H_6-air is about twice that of H_2-air. In these studies, the maximum flame speeds for B_2H_6-air and B_2H_6-0_2 were found slightly on the fuel-rich side of stoichiometric (~6.5 v/o B_2H_6), assuming B_20_3 and H_20 as the products.

The influence of B_2H_6 on the combustion of various hydrocarbons in air and oxygen is reported in Ref. 6.35 through 6.39, and studies of the inhibition of the B_2H_6 oxidation reaction are reported in Ref. 6.40.

"Flammability (explosive) limits" of B_2H_6-OF_2 mixtures in the presence of He or N_2 have been determined (Ref. 6.41) at their respective saturation vapor pressures between 200 to 300 R (111 to 167 K) at total pressures of 100 and 500 psia. With one exception, these mixtures did not react spontaneously within these mixture ratios when held at the experimental temperatures. The one "unexplained" exception where an explosion occurred involved a mixture ratio where the concentrations of OF_2 and B_2H_6 are nearly equal to the ratio of their respective vapor pressures at the experimental temperatures. The data from this study are summarized in Fig. 6.6.

6.1.3 Explosion Hazards

Diborane is insensitive to mechanical shock (Ref. 6.26) and, handled as a normal liquid in the absence of impurities, presents no explosion hazard. However, in the presence of impurities, such as oxygen, water, halogenated hydrocarbons, etc., shock and thermally sensitive mixtures may be formed. In practice, there are two distinct types of explosion hazards that exist with B_2H_6. The first is due to rapid pressure buildup caused by decomposition of B_2H_6 at high temperatures and the second is the potential explosive reaction between B_2H_6 and air.

The decomposition of B_2H_6 is discussed thoroughly in Sections 2.3.2 and 4.1.1. From the data presented in these sections, it is obvious that if cylinders, tanks, lines, systems, etc., containing B_2H_6 are allowed to overheat, overpressurization of the containers can occur resulting in container failure and an "explosive" pressure

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release. The energy of this pneumatic rupture is further enhanced by the probability of an explosive oxidation of the B_2H_6 vapors and decomposition products (e.g., H_2). The rate of pressure rise will be dependent on the decomposition rate (which is a function of temperature and the container material) and degree of confinement. Generally, decomposition rates at room temperature are relatively small and pressure buildup is slow; however, at temperature levels from 200 to 400 F, the rates increase by several orders of magnitude and pressure rise in a confined volume becomes "explosive" in nature.

The explosive oxidation of B_2H_6 has been characterized by several investigators (Ref. 6.34, 6.35, and 6.42 through 6.45) with much disagreement in the results. There appears to be a problem of universal terminology in the discussion of B_2H_6 oxidation studies and the terms of "flammability" and "explosive" are used interchangeably by many investigators. Parker and Wolfhard (Ref. 6.35) determined "limits of flame propagation" of B_2H_6-air (and B_2H_6-ethane-air) mixtures and indicated a "lean explosion limit" at 0.8 v/o B_2H_6 and two "explosion limits" on the rich side at 79 and 87.5 v/o B_2H_6. In measurements of explosion pressures of B_2H_6-air mixtures (ignited by an electric spark) in a closed bomb, the most rapid explosion occurred in a mixture with an equivalence ratio of 1.7. The maximum pressure was achieved at an equivalence ratio of 2.0.

Price (Ref. 6.42), Whatley and Pease (Ref. 6.43), Roth (Ref. 6.44), and Roth and Bauer (Ref. 6.45) conducted extensive studies of the first and second pressure limits of explosion of B_2H_6-air (or oxygen) mixtures in attempts to define the explosion penisula. All studies were in some agreement on the first limit, which occurred around 10- to 15-mm total pressure with little effect of temperature and composition; however, all studies disagreed on the second limit. The effects of diluents and proposed mechanisms were reported in all of the studies. Roth summarizes the work of Ref. 6.42 and 6.43 in Ref. 6.44 as a basis for his studies.

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In the flame speed studies reported in Ref. 6.31 (as discussed in Section 6.1.2), detonations of the B_2H_6-air and B_2H_6-oxygen mixtures frequently occurred after the flame front had burned about 1 meter (3.3 feet). The velocities of these detonations ranged from ~ 2000 to 2600 m/sec (6562 to 8530 ft/sec) as shown in Fig. 6.7.

6.2 HAZARD PREVENTION

As described under Hazards (Section 6.1), spills and leakage of B_2H_6 can result in extreme hazards to both personnel and facilities. The best possible means of avoiding these hazards is to eliminate or minimize the potential cause factors. Effective reduction of leakage, spills, and other potentially hazardous situations can best be accomplished by the use of properly designed equipment and thoroughly trained physically qualified personnel.

6.2.1 System Integrity

The importance of the design integrity of B_2H_6 storage, transfer, and handling systems cannot be overemphasised. The system should be reliable, operationally flexible, and easy to maintain. Although design criteria for facilities and equipment handling B_2H_6 are discussed in Section 4.4, some of the major considerations of system design for hazard prevention are reviewed as follows:

1. Only materials of construction which are definitely known to be compatible with B_2H_6 should be used.
2. The system should be designed and operated in such a manner as to prevent contamination of the system with air, moisture and any other known reactive materials.
3. The number of mechanical joints should be reduced to a minimum, thus reducing the probability of propellant leakage.

4. The system should be designed to withstand the maximum operating pressure safely.
5. The transfer lines should be free of liquid traps.
6. An inert-gas (moisture-free) system must be provided to purge the transfer lines without the necessity of dumping the residual propellant or disconnecting any system joints.
7. The system components must be reliable, compatible with B_2H_6, and properly serviced (cleaned and passivated).
8. Sufficient remotely actuated control equipment must be provided to isolate portions of the system during emergencies or component replacement.
9. The vents should be ducted together and connected to a vapor scrubber, a high vent stack, or a flare stack.

The continual observation of an operational system for possible malfunctions can prevent serious propellant spills.

6.2.2 Physical Examination of Personnel

Personnel having diseases of the kidneys, central nervous system or respiratory system should not work in areas where B_2H_6 is handled. The physician should also exclude personnel having a history or previous serious disease affecting the above systems (Ref. 6.5).

6.2.3 Personnel Education and Training

Properly trained personnel who are thoroughly informed of the hazards that may result from the improper handling of B_2H_6 are required to handle the propellant safely. The fulfillment of this requirement depends largely on the effectiveness of employer education and training, proper safety instruction, intelligent supervision, and correct use of safety equipment. Operating personnel should attend training classes to maintain a proficiency in safe handling techniques and be thoroughly familiar with the following:

1. The nature and properties of B_2H_6
2. Proper methods and handling procedures for B_2H_6 including:
    a. Compatible materials of construction and essential passivation techniques
    b. Operation of flow, transfer, and storage systems
3. Hazards involved from improper handling of B_2H_6
4. Toxicity and physiological effects of B_2H_6 and other boron hydrides
5. Location, purpose, operation, and use of safety equipment and clothing
6. Fire and spill prevention techniques
7. Fire and spill control measures including all emergency actions and procedures
8. Disposal and decontamination techniques
9. Local operating procedures and regulations
10. First-aid and self-aid techniques

No person should be allowed to handle B_2H_6 unless he is thoroughly familiar with the previously listed items and is confident that the propellant can be handled safely with the equipment and facilities available. In addition, all operations should be controlled by a procedures checklist which has been prepared and checked by personnel most familiar with the potential problems. As further safeguards, close supervision should be maintained to ensure adherence to safety practices; and all operations involving the handling of B_2H_6 should be performed by at least two people.

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6.3 HAZARD CONTROL

Because the probability of experiencing a propellant leak or spill at some period in the utilization of B_2H_6 is always present, personnel should be thoroughly educated as to the potential effects of such leaks or spills and trained in their effective control. Additionally, because a B_2H_6 leak or spill represents a multiplicity of hazards in that it can result in a fire, explosion, or become a source of intoxication to personnel, the time period between the inception of the hazardous situation and initiation of control action should be reduced to a minimum. The continual observation or monitoring of an operational B_2H_6 storage and handling system for possible malfunctions, instantaneous detection of such a malfunction, and immediate remedial action are the most effective means of controlling the severity of B_2H_6 leaks or spills. This can be accomplished through proper planning, training, and organization. The following items should be considered in the administration of the B_2H_6 storage and handling areas:

1. The facility should be designed for maximum access to the system.
2. All B_2H_6 storage and handling systems and related equipment should be protected by an approved type water sprinkler system.
3. Continuous or semicontinuous monitoring leakage detection devices should be installed at strategic locations.
4. Periodic system checks should be made for indications of failures or malfunctions.
5. Safe areas, access routes, and evacuation routes should be established.
6. Hazard control procedures should be pre-established.
7. Periodic drills should be performed to ensure personnel proficiency during emergency operations.

8. A minimum of two operating personnel should wear protective clothing and equipment during all propellant handling operations.

6.3.1 Hazard Detection

A noted previously, the early detection of a B_2H_6 leak is the primary step in effective control. Although a large B_2H_6 leak or spill will probably result in an immediately detectable fire or explosion, a small leak may oxidize slowly without combustion or readily detectable flames. The detection of this type of leak, which may be indicative of, or lead to, a more massive failure, is the primary concern in the protection of facilities and personnel from fire, explosion, and toxic hazards.

Although the median detectable concentration of B_2H_6 odor by man is relatively low, and small concentrations can be tolerated for short periods (See Section 6.1.1), planned use of this means should be prohibited. Wherever possible, B_2H_6 storage and handling areas should be monitored with selective vapor detectors in conjunction with an alarm system. The design of such a system depends on the particular area and on the degree of control required for that area. Detection of B_2H_6 in an area either by instruments or personnel should be taken as an indication that immediate repairs to the system are necessary and essential.

Chemical and electronic devices are available to determine boron hydride concentrations in air below the explosive range and below the threshold limit for B_2H_6. However, since large-scale propulsion industry experience with B_2H_6 has been somewhat limited, no B_2H_6-selective instrument is currently available (Ref. 6.6). Mine Safety Appliances Company, in conjunction with Callery Chemical Company, has developed and recommends the use of two instruments for detecting very low atmospheric concentrations of various boron hydrides (Ref. 6.5), the M-S-A Billion-Aire Detector and the M-S-A Portable Borane Detector. These devices, which are currently used by most organizations handling B_2H_6, as well as other techniques that have been developed and used previously are described in the following paragraphs.

6.3.1.1 Mine Safety Appliance (M-S-A) Billion-Aire Detector. The M-S-A Billion-Aire apparatus was designed (Ref. 6.46) to monitor (periodically or semicontinuously) air which may be contaminated with boron hydrides so that a hazard evaluation can be made. This instrument, which is rather large and nonportable, consists of a radio-active source which ionizes a sample of air from the environment. A steady ion current is produced unless a contaminant is present; contaminants react with reagents in the machine to form aerosols which change the ion current. This change is then a measure of the concentration of contaminant. This instrument is sensitive to any materials which affect the ion mobility or quantity. This device is capable of detecting contaminants in the range of parts per billion to parts per million.

6.3.1.2 Mine Safety Appliances (M-S-A) Portable Borane Detector. The M-S-A Portable Borane Detector (or pump kit) is a calorimetric spot test instrument for detecting and measuring concentrations of contaminants in the atmosphere. The number of pump strokes required to change the color of a sensitive reagent on a specially treated piece of filter paper is a measure of contaminant concentration. This device is capable of detecting B_2H_6 or other reducing agent concentrations as low as 0.1 ppm. These instruments have no remote readout and are affected by many interfering substances (including N_2H_4 and sunlight) which may change the color of the sensor material. Rocketdyne uses this instrument at its Reno, Nevada Site after a run to manually check that the area is safe for re-entry.

6.3.1.3 Other Detection Devices. Several other detection techniques and devices for B_2H_6 have been studied and/or previously used. These techniques, which are summarized in Ref. 6.21, include the reduction of $AgNO_3$ as a colorimetric technique (Ref. 6.48), a titrimetric technique employing oxidation by bromines (Ref. 6.49), a chemical thermoelectric detector (Ref. 6.50 and 6.51), an automatic coulometric titration (Ref. 6.52), and an iodiometric procedure (Ref. 6.53). In addition, an amperometric technique was developed (Ref. 6.54) and used by Olin Mathieson in portable and semicontinuous monitoring detectors at their former production facilities (See Section 3.1.3).

General Dynamics in their study (Ref. 6.6) of requirements for pre-launch operations involving B_2H_6 recommends the development of a new detector to meet the following requirements:

Range of Concentration Detected	0.1 to 100,000 ppm by volume B_2H_6
Accuracy	±10 percent of full scale or 25 percent of reading, whichever is less
Selectivity	Sensitive only to reducers with reduction potention less than B_2H_6
Sensitivity	0.1 ppm B_2H_6
Precision (repeatibility)	±10 percent of reading, 0.1 ppm B_2H_6
Portability	Weight--5 pounds or less exclusive of batteries Size--0.25 cu ft or less exclusive of batteries
Ambient Conditions	Not affected by, or compensated automatically for temperature, wind, and humidity changes
Response Time	95 percent full scale in 10 seconds
Readout	Remotely to 3000 feet
Construction	Solid state electronics, explosion proof, sealed

6.3.2 Leakage and Spill Control

Upon detection of a B_2H_6 leak or spill, the most effective control can be provided by immediate performance of the following steps in the order listed:

1. Stop any propellant transfer or handling operation
2. Isolate the propellant tank from the transfer lines and all pertinent sections of the handling system by closing the necessary valves (by remote control if possible)
3. Locate the source of the leak or spill
4. Isolate the affected components by closing the necessary valves
5. Dispose of the spilled propellant and the propellant remaining in the affected components
6. Replace or correct the malfunctioning component

The performance of the first four steps should be automatic and can be performed in a very short period of time.

The disposition of spilled propellant is not of prime concern, because as a highly volatile compound, it will evaporate very rapidly. Therefore, the primary concern with the leaking propellant is the control of its toxic hazard and of fire and explosion. The action taken depends greatly on several factors such as quantity of the propellant spilled, prevailing weather conditions, location of the storage and/or handling area, etc. In most cases involving small leaks, control can be effected by burning the B_2H_6 vapors or by hosing with copious quantities of water (which results in its hydrolysis to $B(OH)_3$ and H_2). All downwind areas should be monitored for toxic vapors and suitable protective measures taken. The B_2H_6 vapor should eventually hydrolyze and/or oxidize to less harmful species.

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The disposal of the B_2H_6 remaining in the affected components is discussed in Section 4.5.4.

6.3.3 Fire and Explosion Control

Although B_2H_6 is not technically regarded as a pyrophoric (or spontaneously ignitable) fuel at room temperature, it is easily ignited by a static spark, heat of reaction, heat of absorption, or the spontaneous ignition of one of its thermal decomposition products (Ref. 6.5). In addition, its combustion can be sustained over a wide range of conditions varying from extremely rich to extremely lean limits (See Sections 6.1.2 and 6.1.3). These factors together with its high flame and detonation speeds indicate that leaks or spills of B_2H_6 will usually result in fires (with possibility of an explosive initiation if combustion of the fuel-air mixture is delayed), and that such fires are difficult (if not impossible) to extinguish. Although an explosion of the B_2H_6-air mixture may occur in initiation of the combustion, any subsequent burning of B_2H_6 is usually smooth.

In control of conventional fuel fires, it is an accepted practice to cool the burning fuel below the ignition temperature, exclude the air necessary for the combustion process, cut off the fuel supply, and prevent the spread of fire to adjacent areas. Although these principles can be applied generally to B_2H_6 fires, the toxic, flammable, and explosive characteristics of B_2H_6 present a judgment as to whether it is better to (1) extinguish the fire, or (2) control the fire and let the fuel burn until it is depleted (6.21). The general conclusion is that the best way to fight a B_2H_6 fire is to let it burn itself out if damage to surrounding structures can be minimized. This method avoids the problems of reignition, toxicity, and decontamination of the spill area.

Limited hazard control tests have been conducted with various fire extinguishing agents to determine the best techniques for combating B_2H_6 fires. Most of the common agents such as carbon dioxide, dry chemicals, foams, water, and water fog have been used with varying degrees of success against B_2H_6 fires. Of these, probably the most effective agent is water fog. This agent performs the functions of containing the fire, hydrolyzing the residual B_2H_6, and washing down the B_2O_3 cloud produced by the combustion.

Carbon dioxide may be used to suppress small fires (e.g., around a leaking fitting, etc.) until line valves can be closed to eliminate the fuel supply to the fire. The dampening effect lasts only as long as the CO_2 is present and reignition usually occurs. It is ineffective against larger fires and may even react slightly (Ref. 6.6).

Because B_2H_6 rapidly evaporates to a gas at room temperature, dry chemicals and foams are ineffective. In addition, both of these agents may create a lingering hazard of encapsulating B_2H_6 bubbles. When distrubed, the residual material can release the B_2H_6 resulting in additional fire, explosion, and toxic hazards.

The use of halogenated hydrocarbon extinguishers, such as carbon tetrachloride (CCl_4) and certain Freon-type extinguishing agents, is prohibited. These compounds form impact sensitive mixtures with B_2H_6 (Ref. 6.26 and 6.29).

WARNING

DO NOT USE CARBON TETRACHLORIDE

Halogenated hydrocarbons form impact sensitive mixtures with B_2H_6.

In summary, B_2H_6 fires are controlled only from the point of view of preventing facility damage. Such damage resulting from B_2H_6 fires can be reduced significantly, or eliminated, as follows:

1. The facility must be designed as fireproof as possible.
2. The area must be maintained clean, uncluttered, and free of combustible materials.
3. The facility must be equipped with a properly designed water deluge system, preferably of the high-pressure fog-type systems.
4. The B_2H_6 storage and handling system should be isolatable by section, wherever possible, to limit the quantities resulting from a spill.

Whenever B_2H_6 catches fire, the fire should be kept under control by water fog, but should not be extinguished if it can be controlled, unless the source of B_2H_6 is depleted. (If the fire is extinguished, an explosive B_2H_6-air mixture might accumulate.) The fire should be localized and contained with deluge systems augmented with water spray to prevent its spread to surrounding facilities. The conventional use of dry chemicals and CO_2 can also be used on surrounding facilities to prevent the fire spread. Personnel engaged in fighting fires of B_2H_6 or B_2H_6-containing materials should use respiratory equipment in addition to all other equipment required for fighting fires. In the cases of a B_2H_6 fire in an enclosed area, self-contained breathing equipment is mandatory.

6.3.4 Decontamination

After a B_2H_6 spill or fire is controlled, the residual B_2H_6 (if any) and reaction products must be disposed of and the area, equipment, and involved personnel decontaminated. This decontamination primarily involves the conversion of any residual B_2H_6 to less

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harmful products and the removal of these products. All decontamination steps should be conducted by personnel in the appropriate protective clothing.

The area can be decontaminated by washing with a water solution containing a mixture of 5-percent ammonia and 5-percent O-B detergent (e.g., trisodium phosphate). After allowing the solution to stand for a short (30 to 60 minutes) period of time, the materials should be washed into an approved drainage system with copious amounts of water. Any boric oxide and/or boric acid formed during the fire and subsequent application of water can also be flushed readily with water.

Equipment that is removed from the system should also be decontaminated prior to handling, renovation, reuse and/or scrapping. This can be accomplished by immersion of the contaminated portions of the equipment in water or a water-methanol solution for a short period of time. The equipment should then be flushed with water, acetone, and dried thoroughly (also see Section 4.5.4).

Any personnel involved in fighting the fire or who have been exposed to the smoke or residual solutions resulting from the fire control procedures should also be decontaminated immediately. Any clothing should be removed and laundered prior to reuse. Body areas in contact with the contaminated clothing should be thoroughly scrubbed with a 3-percent aqueous solution of ammonia followed by soap and water. Respiratory protection should be continued until the contaminated clothing is removed and the body has been washed.

6.4 FACILITY AND PERSONNEL PROTECTION

6.4.1 Safety Equipment

The toxic, reactive, and pyrophoric properties of B_2H_6 dictate the need for adequate safety equipment to protect operating personnel and facilities. It should be recognized that the effectiveness of the equipment depends on the type of personal safety equipment selected for a given situation, which must be consistant with the potential hazard, e.g., liquid impingement, vapor inhalation, etc., and on instruction and supervision in the proper use of this equipment. The category of safety clothing required for a given job must be specified at the time it is assigned. Preferably, written job instructions should be given to ensure effective communication and agreement between operating personnel and responsible safety personnel.

6.4.1.1 Facility Safety Equipment. Equipment for facility protection should consist of safety showers, eye baths, a water deluge system (preferably of the fog type), fire blankets, portable fire extinguishers, fire hoses, vapor detectors (See Section 6.3.1), and first-aid kits. This equipment should be strategically located and easily accessible. A shower installation for personnel decontamination is also extremely important because it provides assurance that no B_2H_6 contamination is carried away from the hazard areas.

All operating personnel should be thoroughly familiar with the location and operation of each piece of safety equipment. The operating condition of the equipment must be verified periodically.

6.4.1.2 Personnel Protective Equipment. All personnel in the B_2H_6 handling and storage areas must wear flame-retardant clothing at all times. In addition, all personnel performing propellant transfer operations should wear fully protective personnel equipment. If the operations are performed remotely, it is still recommended that at least two operating personnel be fully protected to facilitate proper spill and fire control. It must be remembered that personal protective equipment protects only the man wearing it. A borane vapor detector (See Section 6.3.1) should be used to determine vapor concentration present in the area prior to removal of protective equipment.

6.4.1.2.1 Respiratory Protection. Respiratory devices must be a part of the safety clothing for all personnel who might be exposed to boron hydride vapors. Because of the high toxicity of the boron hydrides, chemical cartridge and mechanical respirators should not be used. For exposure to high concentrations, gas masks, air masks, or self-contained breathing apparatus are recommended. All respiratory protective equipment must have a full face piece to provide eye protection and should be approved for boron hydride use by the U.S. Bureau of Mines.

The universal gas mask can be used for protection against low concentrations of B_2H_6 for a limited period of time. However, because the odor of B_2H_6 cannot be detected in concentrations below its threshold limit, no dependence can be placed on odor as an indication that the canister is exhausted. Thus, the canister must be changed at regular intervals depending on the extent of use as determined by operating experience. In constant use this interval is approximately 4 weeks (Ref. 6.26), although the canister must be changed immediately if any odors are detected. The mask should be used by any personnel working in the operating area where B_2H_6 is being sampled, vented, or transferred (Ref. 6.5). Their use has also been reported (Ref. 6.5 and 6.29) in combination with supplied-air masks for entering and leaving supplied air cases.

Air-line masks which depend on a remote air supply are acceptable for B_2H_6 use but should only be used where conditions permit safe escape in the event of air supply failure (Ref. 6.5 and 6.29). The blower or compressor must be located in a safe area, and the supplied air must not contain lubricating oil or its decomposition products. The safer method is to use a separate compressor of the type not requiring internal lubrication. Suitable pressure valves, traps, and filters must be installed at all mask stations. An alternate arrangement frequently used is high-pressure breathing air from standard cylinders with a demand-type valve and face piece

(Ref. 6.29). A reliable safety equipment dealer should be consulted for further details on the proper use of Bureau of Mines approved equipment.

A self-contained breathing apparatus, which is recommended under conditions of extreme exposure, allows complete mobility for the wearer by eliminating the need for hoses (Ref. 6.5 and 6.29). This apparatus can be of two types: the oxygen is either generated chemically or the oxygen is supplied from cylinders. An example of the oxygen-generating type is the MSA Chemox Oxygen-Breathing Apparatus, which provides complete respiratory protection for a minimum of 45 minutes of hard work (Ref. 6.5). Oxygen-supplied masks utilize oxygen from cylinders, either worn by the user for short periods (about 10 minutes), or connected to the mask by a hose for longer periods (an example is the M-S-A Demand Work Mask) (Ref. 6.5). Compressed oxygen should not be used where there is danger of contact with flammable liquids, vapors, or sources of ignition, particularly in confined areas.

6.4.1.2.2 Head and Face Protection. Hard hats or head coverings which cannot be penetrated by boron hydrides (Gra-lite, for example) are recommended. Cloth coverings should be avoided because leaks may penetrate.

Safety glasses with side shields (and prescription-ground lenses when appropriate) should be used where continuous eye protection is required. Full-length plastic face shields (8-inch minimum length) with forehead protection should be worn in addition to safety glasses when complete face protection is necessary (Ref. 6.5 and 6.55).

6.4.1.2.3 Foot Protection. Safety shoes with built-in steel toe caps are recommended (Ref. 6.5 and 6.29). Rubber or neoprene boots or shoe coverings should be used in areas that may be contaminated, such as loading areas (Ref. 6.5, 6.29, and 6.55). Although rubber and neoprene coverings will be attacked by high concentrations of boron hydrides, they will provide adequate protection for emergencies and can then be discarded (Ref. 6.55).

6.4.1.2.4 Skin Protection. All personnel who may come in contact with B_2H_6 must be provided with protective clothing that is impervious to the propellant. Flame-proofed coveralls made of Gra-lite and neoprene-dipped or Gra-lite gloves are suggested (Ref. 6.6 and 6.55). All contaminated clothing must be changed immediately and laundered before reuse. (It should not be sent directly to a commercial laundry but should first be decontaminated in the plant.) As a general hygienic measure, personnel should also wash their hands before lunch or before going home.

6.4.2 First Aid and Self Aid

IF B_2H_6 CONTACTS THE SKIN: The affected areas should be washed immediately with 1- to 5-percent aqueous triethanolamine or with 3-percent aqueous ammonium hydroxide, followed by soap and water. All contaminated clothing should be promptly removed and laundered thoroughly before reuse. If burns are present, refer to a physician.

IF B_2H_6 CONTACTS THE EYES: The eyes should be flushed immediately and freely with water for at least 15 minutes and medical assistance should be obtained. If it is necessary to choose between flushing with water and seeking help, flush for 10 minutes and then seek help.

IF B_2H_6 (SOLUTIONS) ARE INGESTED: Every effort should be made to induce vomiting by administering large quantities of salt water or baking soda solution. A physician must be called immediately.

IF B_2H_6 VAPORS ARE INHALED: The exposed individual should be removed immediately from further exposure, kept quiet, and be placed

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in the care of an authorized physician as soon as possible. If breathing stops, artifical respiration (or oxygen) should be administered. If indications of intoxication are observed, oxygen should be administered by mask for periods up to 1 hour. Bed rest is essential to rapid recovery of more severe cases and should be enforced judiciously. Never attempt to give anything by mouth to an unconscious patient.

6.4.3 Medical Treatment

IN ALL CASES OF EXTREME EXPOSURE OR CONTACT, A PHYSICIAN SHOULD BE NOTIFIED. The physician should be previously informed and educated as to the symptoms and treatment of B_2H_6 intoxication.

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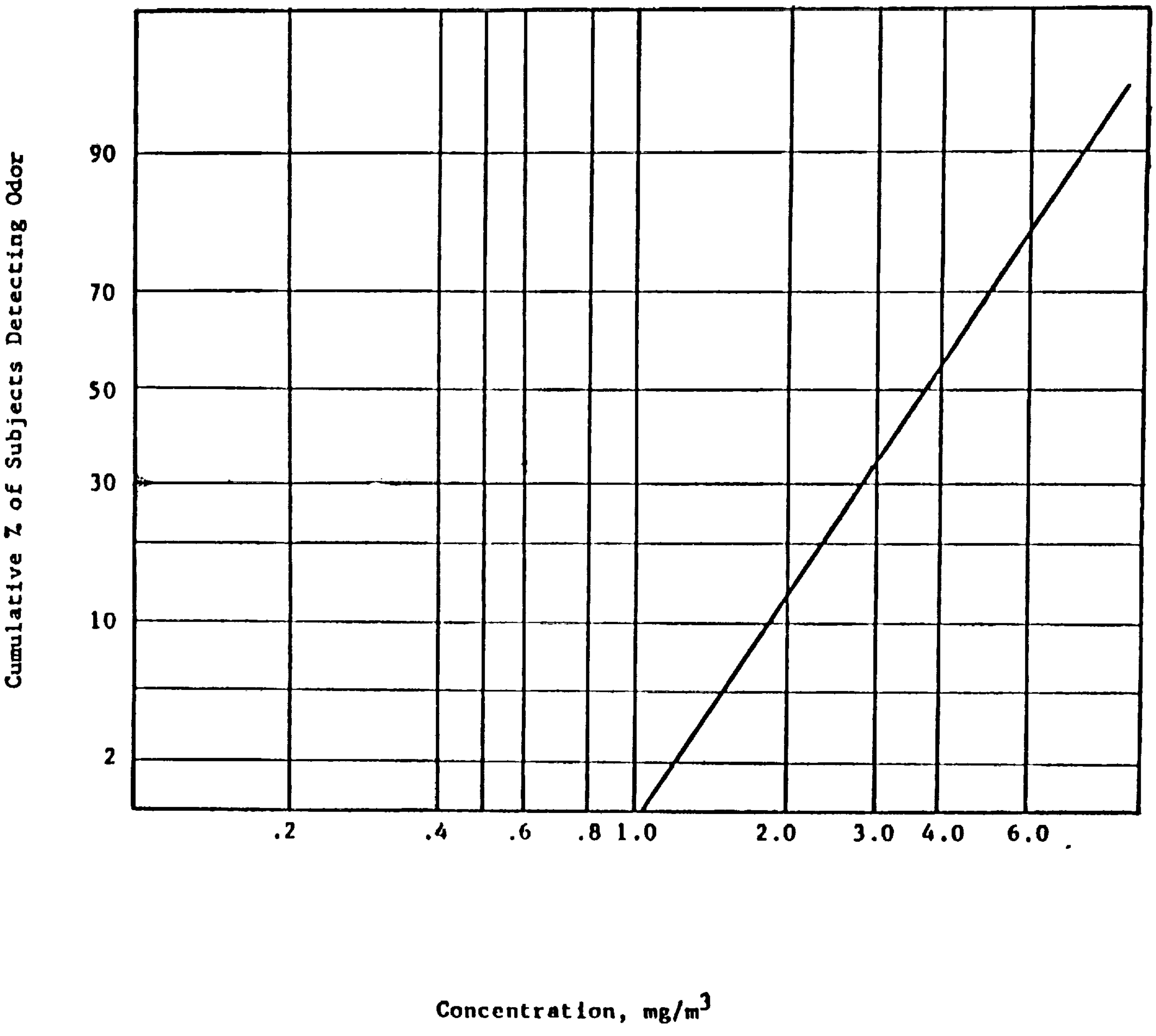


Figure 6.1. The Median Detectable Concentration of Diborane by Odor (Reprinted from Ref. 6.5 from Experimental Data of Ref. 6.23)

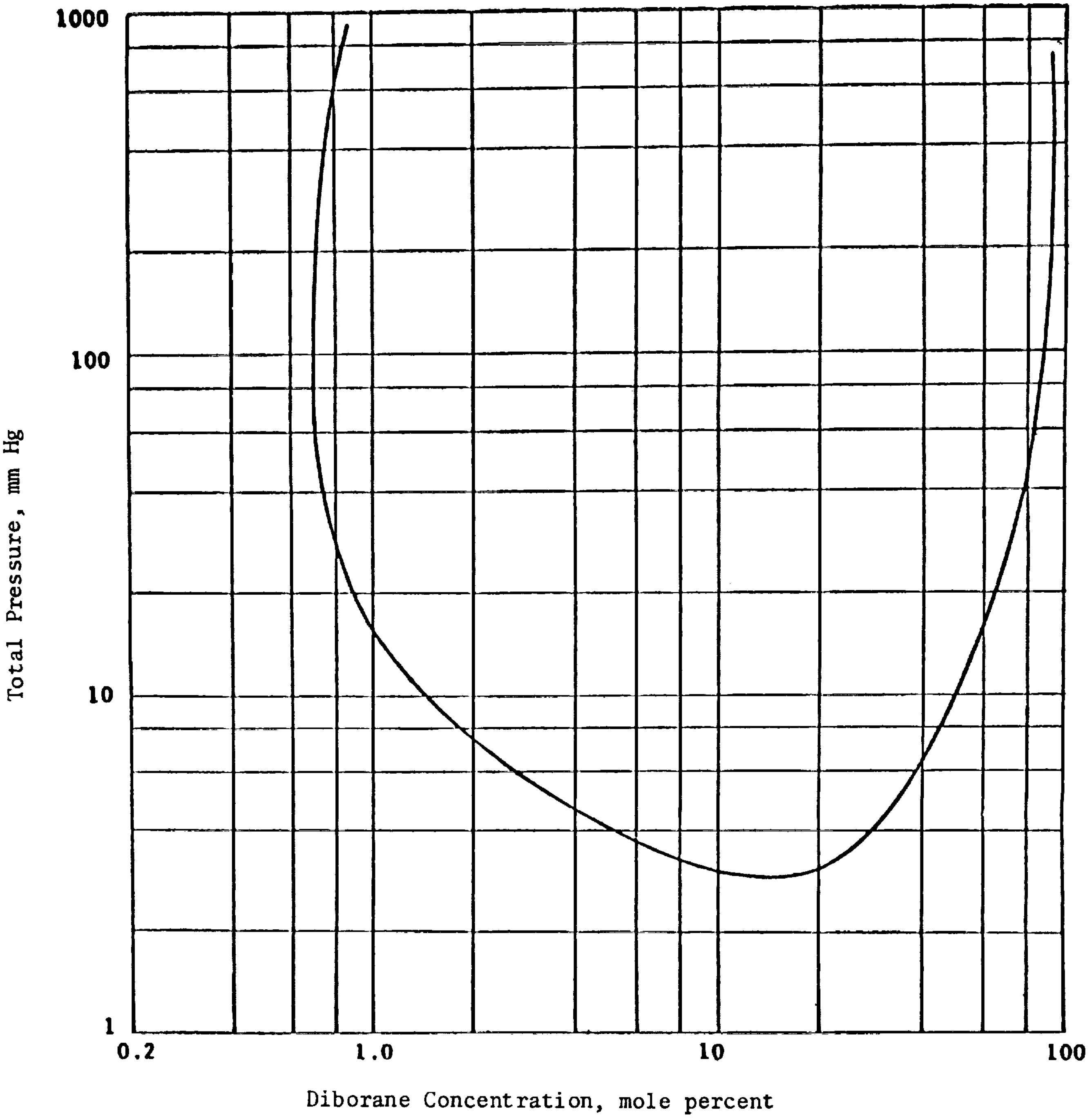


Figure 6.2. Flammability Limits of Diborane in Air (Reprinted From Ref. 6.5 From Data of Ref. 6.32)

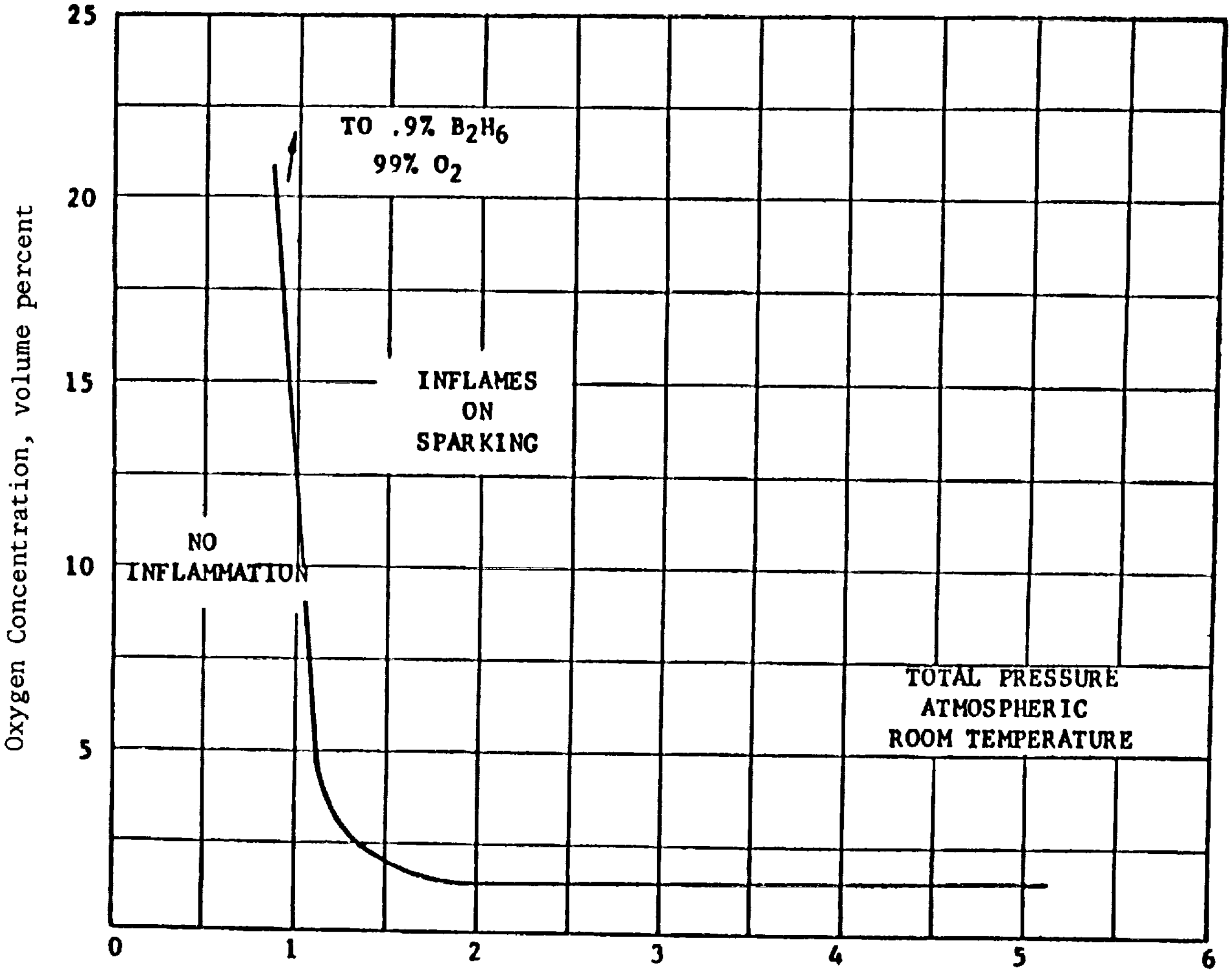


Figure 6.3. Flammability Limits of Diborane and Oxygen (Reprinted From Ref. 6.5 From Data of Ref. 6.31)

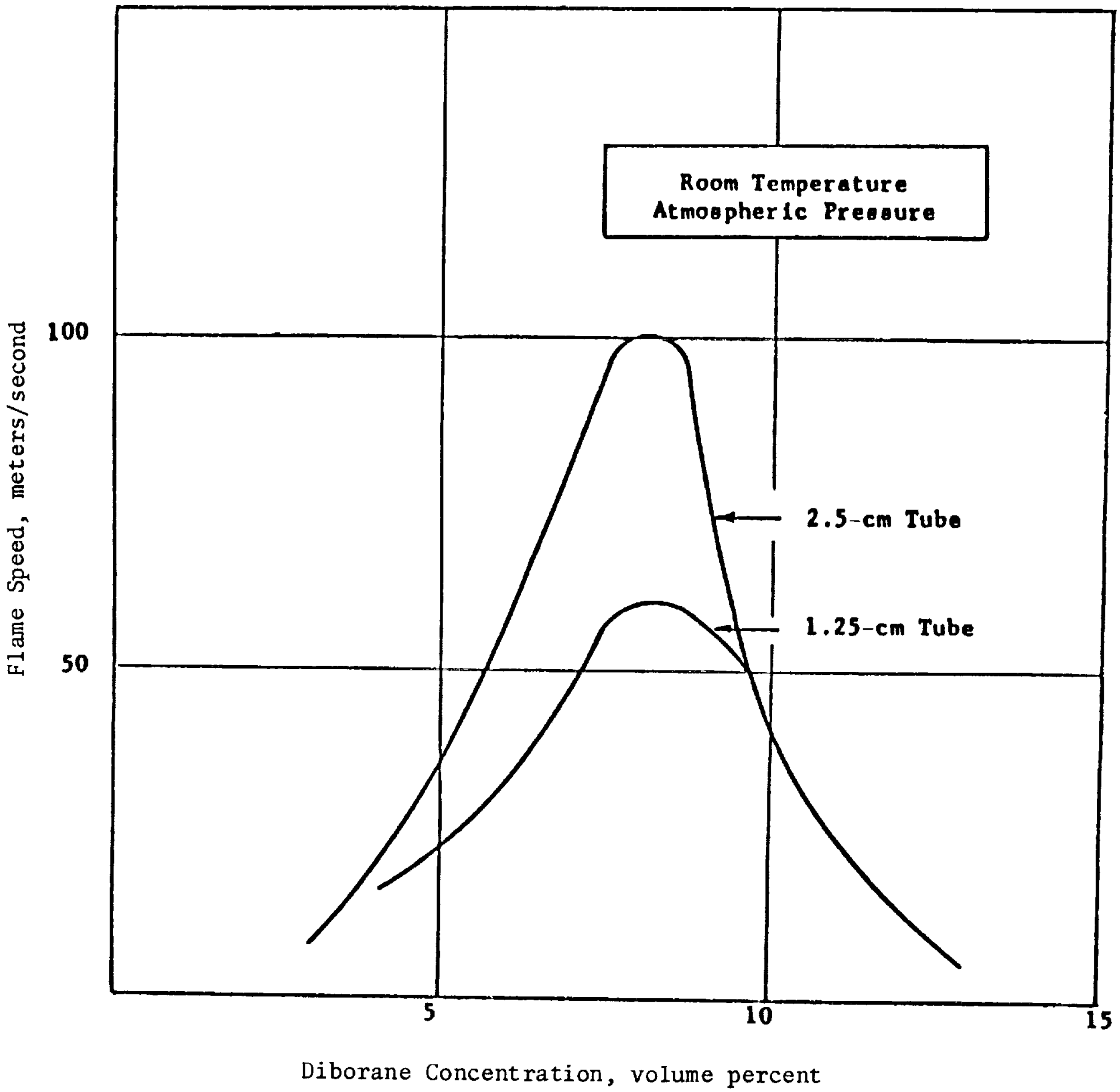


Figure 6.4. Initial Flame Speeds of Diborane-Air Mixtures (Reprinted From Ref. 6.5 From Data of Ref. 6.34)

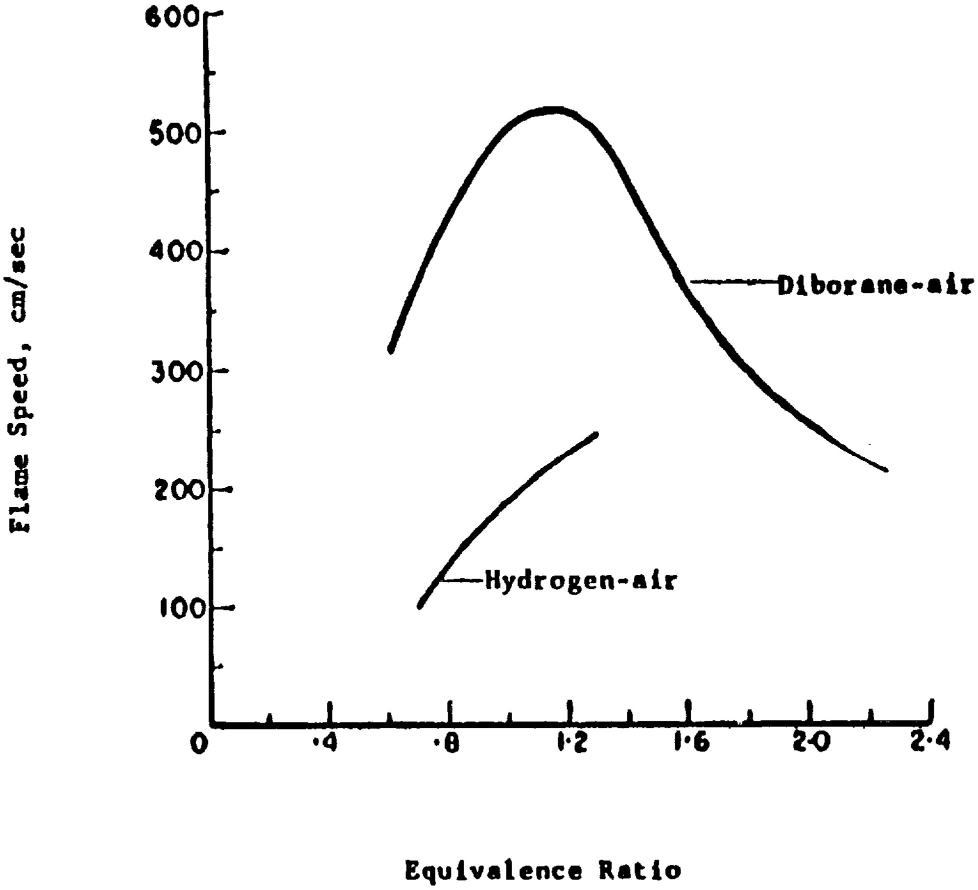
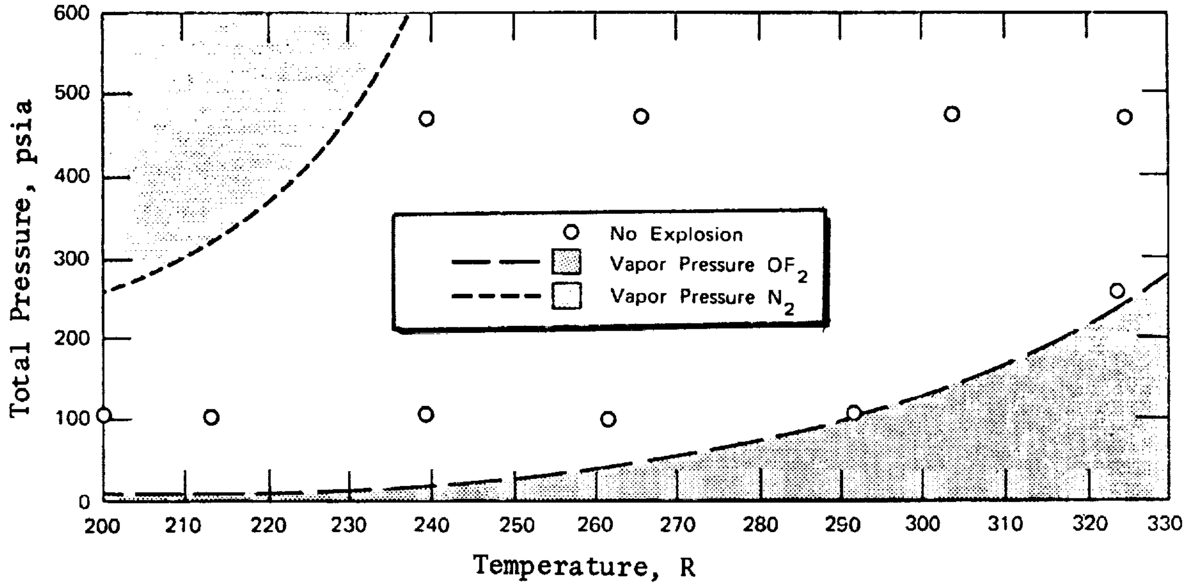
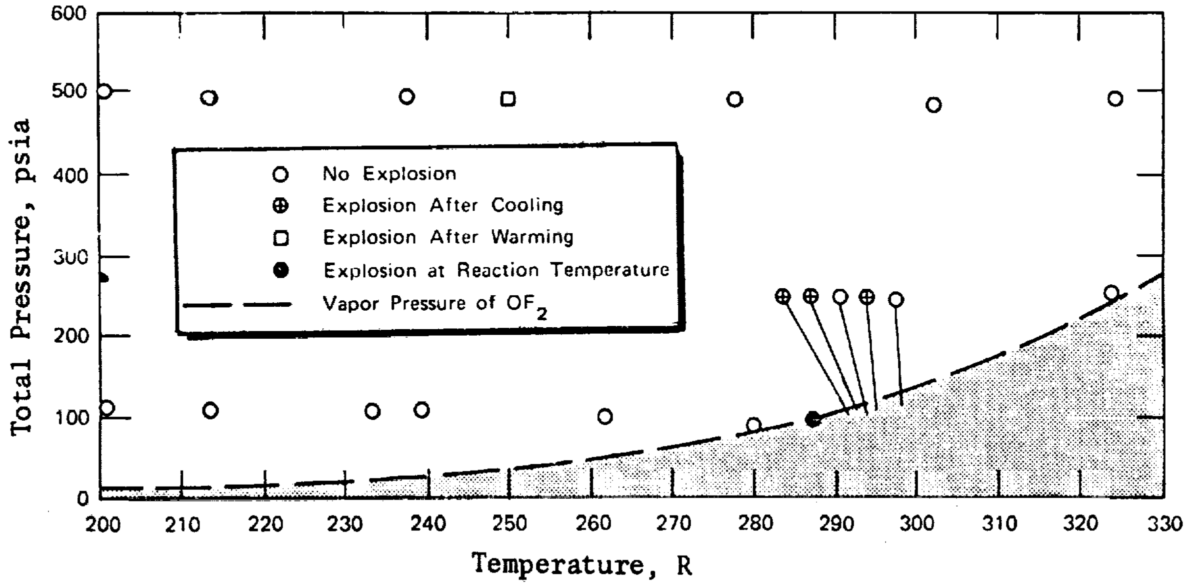


Figure 6.5. Flame Speed of Diborane and Hydrogen With Air (Reprinted From Ref. 6.5 From Data of Ref. 6.33)



$OF_2/B_2H_6/N_2$ System



$OF_2/B_2H_6/He$ System

Figure 6.6. "Flammability" of the OF_2/B_2H_6 System Under Conditions of Saturated Vapor Pressures of the Two Components and Inert Pressurizing Gas (Reprinted From Ref. 6.41)

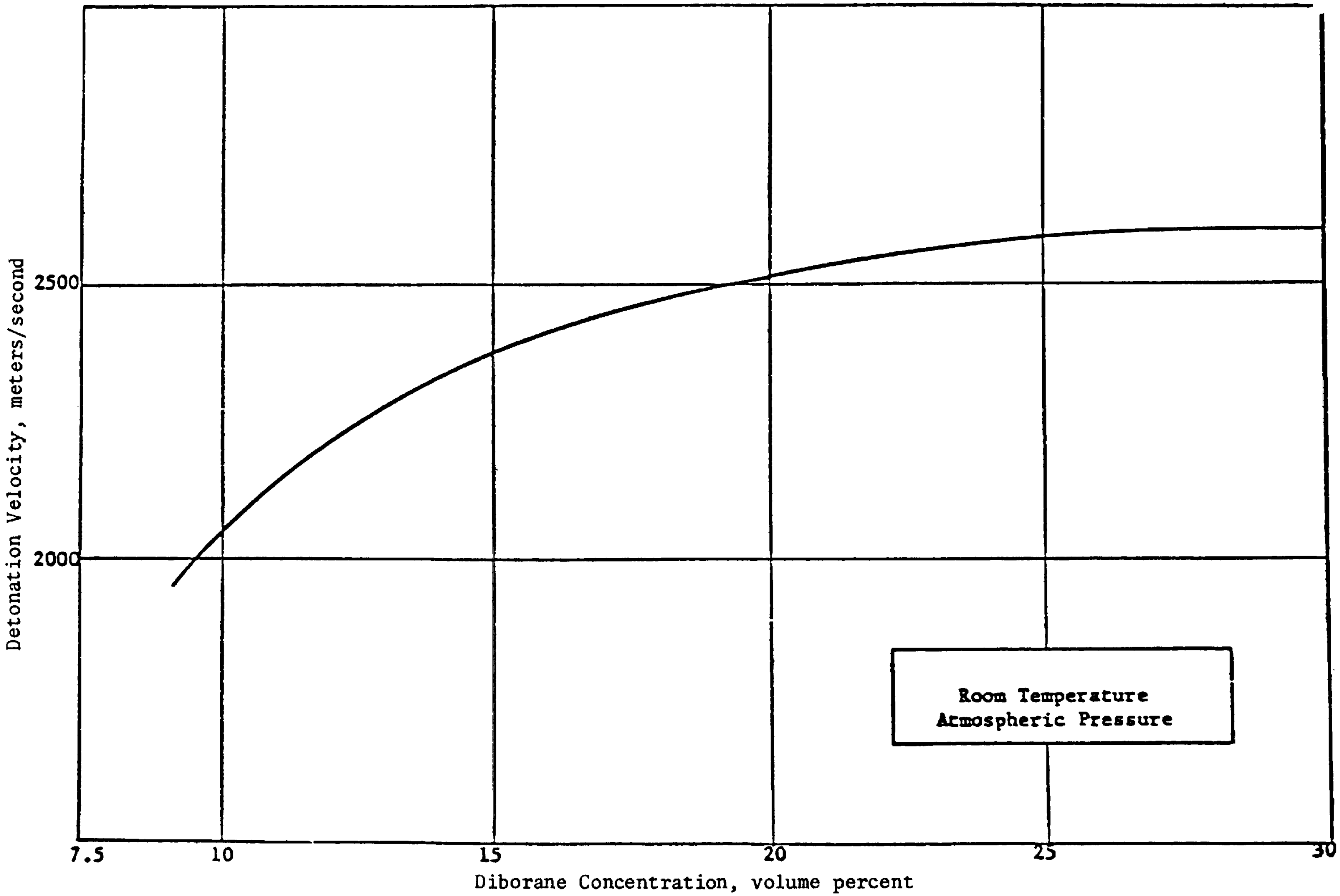


Figure 6.7. Detonation Velocities of Diborane-Oxygen Mixtures (Reprinted From Ref. 6.5 From Data of Ref. 6.34)

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In addition to the references actually used in compilation of the data in this handbook, which are listed at the end of each section, many other papers and reports were reviewed. All papers and reports are listed below in alphabetical order by either organization (for any organizational publication) or author (for a journal article):

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