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AMC PAMPHLET

AMCP 706-187

ENGINEERING DESIGN HANDBOOK

MILITARY PYROTECHNICS SERIES

PART THREE — PROPERTIES OF MATERIALS USED
IN PYROTECHNIC COMPOSITIONS



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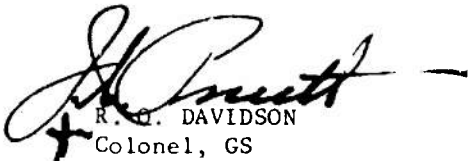
AMCP 706-187, Part Three--Properties of Materials Used in Pyrotechnic Compositions, forming part of the Military Pyrotechnics Series of the Army Materiel Command Engineering Design Handbook Series, is published for the information and guidance of all concerned.

(AMCRD)

FOR THE COMMANDER:

SELWYN D. SMITH, JR.
Major General, USA
Chief of Staff

OFFICIAL:

A handwritten signature in dark ink, appearing to read "R. G. Davidson", with a horizontal line extending to the right.

R. G. DAVIDSON
Colonel, GS
Chief, Administrative Office

DISTRIBUTION:
Special

PREFACE

This handbook constitutes Part Three of a planned series on Military Pyrotechnics and forms part of the Engineering Design Handbook Series of the Army Materiel Command. Part Three is devoted to the presentation of data on the principal ingredients of pyrotechnic compositions. The information is presented on data sheets, representing a total of 128 ingredients. The data presented here have been collected from many sources and are intended to facilitate reference and the making of calculations by chemists, engineers and physicists in the field of pyrotechnics. A single reference list, showing the main sources of data, is included and each reference is keyed in by number to appropriate entries on the data sheets. References that pertain only to a specific data sheet are listed at the end of the data sheet under Additional References.

Part Two, a separate handbook with the same date of publication, deals with the problems of safety in the pyrotechnics laboratory and plant, processing procedures and equipment, particle size procedures, and contains a glossary of terms.

Part One, under preparation at the time of publication of Parts Two and Three, will deal with the physical and chemical theoretical aspects of the production of pyrotechnic effects, and the application of the theory to practice. It will also include a history of the pyrotechnic art and an extensive bibliography.

A future volume, currently in the planning stage, will be devoted to discussion of methods used in the evaluation of pyrotechnic items, determination of their compliance with the requirements of the using services, special equipment and procedures which are followed in tests and evaluation, and considerations affecting the interpretation of results.

Material for Parts Two and Three was prepared by McGraw-Hill Book Company for the Engineering Handbook Office of Duke University, prime contractor to the Army Research Office--Durham. The entire project was under the technical guidance of an interservice committee, with representation from the Army Chemical Center, Ballistics Research Laboratories, Frankford Arsenal, Harry Diamond Laboratories, Picatinny Arsenal, U. S. Naval Ammunition Depot (Crane), U. S. Naval Ordnance Laboratory, and U. S. Naval Ordnance Test Station. Chairman of this committee was Mr. Garry Weingarten of Picatinny Arsenal.

Agencies of the Department of Defense, having need for Handbooks, may submit requisitions or official requests directly to Equipment Manual Field Office (7), Letterkenny Army Depot, Chambersburg, Pennsylvania. Contractors should submit such requisitions or requests to their contracting officers.

Comments and suggestions on this handbook are welcome and should be addressed to Army Research Office--Durham, Box CM, Duke Station, Durham, North Carolina 27706.

TABLE OF CONTENTS

	<u>Page</u>		<u>Page</u>
PREFACE	i	Calcium Silicide	84
ABBREVIATIONS AND SYMBOLS	iv	Calcium Stearate	86
REFERENCES	x	Carbon Black (Dry) and Lampblack . . .	88
DATA SHEETS		Carbon Tetrachloride	91
Acetone	1	Castor Oil	94
Alcohol	4	Chromic Acid	96
Aluminum	8	Chromic Oxide	99
Aluminum Oxide	12	Cobalt Nnphthenate	103
1-Aminoanthraquinone	16	Copper	105
Ammonium Nitrate	18	Cuprous Oxide	109
Ammonium Perchlorate	23	Dechlorane	112
Anthracene	26	Dextrin	114
Antimony Sulphide	28	1,4-Diamino 2,3-Dihydroanthraquinone	116
Asphaltum	30	Diatomaceous Earth	117
Auramine Hydrochloride	32	Dibutylphthalate	114
Barium Carbonate	34	1,4-Di(Methylamino)Anthraquinone . . .	121
Barium Chlorate	37	4-Dimethylan~inoazobenzene	123
Barium Chloride	39	2-(4-Dimethylaminoazophenyl)Naphthalene	125
Barium Chromate	41	Diphenylamine	127
Barium Nitrate	43	Ethylcellulose	129
Barium Oxalate	45	Ferric Oxide	131
Barium Oxide	47	Ferrosoferric Oxide	135
Barium Perchlorate	51	Ferrous Sulfide	138
Barium Peroxide	53	Graphite	140
Benzanthrone	56	Gum Arabic	143
Black Powder	58	Gum Tragacanth	145
Boron	61	Hexachlorobenzene	146
Calcium	64	Hexachloroethane	148
Calcium Carbonate	68	Indanthrene Golden Yellow G.K.(Spec.	
Calcium Nitrate	71	name)	150
Calcium Oxalate	73	Kerosene	151
Calcium Oxide	75	Lactose	153
Calcium Perchlorate	78	Laminac 4116	157
Calcium Phosphide	80	Lead Chromate	159
Calcium Resinate	82	Lead Oxide (PbO)	161

TABLE OF CONTENTS (cont'd)

	<u>Page</u>		<u>Page</u>
Lead Oxide (Lead Tetraoxide)	166	Shellac	254
Lead Peroxide	169	Silicon	256
Lead Sesquioxide	171	Silicon Dioxide	259
Linseed Oil	173	Sodium	266
Lithium	175	Sodium Bicarbonate	270
Lithium Nitrate	179	Sodium Nitrate	272
Lithium Perchlorate	181	Sodium Oxalate	274
Lupersol DDM	183	Sodium Oxide	276
Magnesium	185	Stearic Acid	279
Magnesium-Aluminum Alloy	189	Strontium Chloride	281
Magnesium Carbonate	191	Strontium Nitrate	283
Magnesium Oxide	193	Strontium Oxalate and Monohydrate	285
Manganese	196	Strontium Perchlorate	287
Manganese Dioxide	201	Strontium Peroxide	288
1-(2-Methoxyphenylazo)-2-Naphthol	204	Sugar	291
1-Methylaminoanthraquinone	206	Sulfur	294
Molybdenum	208	Tetranitrocarbazole	299
Molybdenum Trioxide	211	Thiokol	302
Nickel	214	Titanium	303
Nitrocellulose	218	Titanium Dioxide	307
Parlon	221	Toluidine-Red Toner	311
Phosphorus	223	1,4-di-p-Toluidinoanthraquinone	313
Pluronic, F 68	228	Tungsten	315
Polychlorotrifluoroethylene	229	Tungsten Dioxide	318
Polytetrafluoroethylene (Teflon)	232	Zinc	320
Polyvinylchloride	236	Zinc Carbonate	323
Potassium	238	Zinc Oxide	325
Potassium Bicarbonate	241	Zinc Stearate	329
Potassium Chlorate	243	Zirconium	331
Potassium Nitrate	246	Zirconium Hydride	335
Potassium Oxide	249	Zirconium-Nickel Alloy	337
Potassium Perchlorate	251		

ABBREVLATIONS AND SYMBOLS*

a.	Angstrom unit(s) length of side (X-ray data) in Angstrom units
abs.	absolute
Acta Chem. Scand.	Acta Chemica Scandinavica (Copenhagen, Denmark)
Acta Cryst.	Acta Crystallographica
addnl.	additional
alc.	alcohol
alk.	alkaline
amor.	amorphous
Anal. Chem.	Analytical Chemistry
Anal. Chim. Acta	Analytica Chimica Acta
Ann. Physik	Annalen der Physik
app.	apparatus
approx.	approximate(ly)
A. S. T. M.	American Society for Testing Materials
at.	atomic
av.	average
atm.	atmosphere(s), atmospheric
<u>b</u>	length of side (X-ray data) in Angstrom units
Ber.	Berichte der deutschen Chemischen Gesellschaft
B. M.	Bureau of Mines, Dept. of the Interior
B. P.	black powder
b. p.	boiling point

*Abbreviations and symbols in the following data sheets generally correspond to those in Chemical Abstracts.

Br. Chem. Abstr.	British Chemical Abstracts
Bull. Am. Ceram. Soc.	Bulletin of the American Ceramic Society
c.	crystal(s)
c	length of side (X-ray data) in Angstrom units
C. A.	Chemical Abstracts
cal.	calories(s)
Can. J. Technol.	Canadian Journal of Technology
cc.	cubic centimeter(s)
Chem. Eng. News	Chemical and Engineering News
c. f. m.	cubic feet per minute
Chem. Eng. Prog.	Chemical Engineering Progress
C. I.	Colour Index (Refs. 48 and 48A)
Chem. Revs.	Chemical Reviews
coeff.	coefficient
compn. (s)	compositions
Compt. rend.	Compte rendus hebdomadaires des Séances de l'Académie des Sciences, Paris, France
concd.	concentrated
concn.	concentration
C. P.	chemically pure
cryst.	crystalline
cu. ft.	cubic foot
d.	density
DDTA	derivative differential thermal analysis
decomp.	decomposes
dil.	dilute
diln.	dilution

DTA	differential thermal analysis
equil.	equilibrium
equiv.	equivalent
est.	estimate
estd.	estimated
f. p. m.	feet per minute
g.	gram(s)
HC	Hexachloroethane Smoke Mixture
HE	high explosive
ICC	Interstate Commerce Commission
I. C. T.	International Critical Tables (Ref. 42)
Ind. Eng. Chem.	Industrial Engineering Chemistry
insol.	insoluble
i. v.	intravenously
J. Am. Chem. Soc.	Journal of the American Chemical Society
J. Am. Ceram. Soc.	Journal of the American Ceramic Society
J. Appl. Polymer. Sci.	Journal of Applied Polymer Science
J. Chem. Phys.	Journal of Chemical Physics
J. Chem. Soc.	Journal of the Chemical Society (London)
J. Colloid Sci.	Journal of Colloid Science
J. Electrochem. Soc.	Journal of the Electrochemical Society
J. Franklin Inst.	Journal of the Franklin Institute (Philadelphia)
J. Phys. Chem.	Journal of Physical Chemistry
J. Research NBS	Journal of Research of the National Bureau of Standards
J. Soc. Dyers Colourists	Journal of the Society of Dyers and Colourists
k-	kilo
Kcal.	Kilocalorie

kg.	kilogram
l	liquid
l.	liter(s)
L. D.	lethal dose
liq.	liquid
m., m. ³	meter, cubic meter
M. A. C.	Maximum Allowable Concentration (based on continuous exposure for an 8-hr. day)
manuf. (g)	manufacture, manufacturing
M. C. A.	Manufacturing Chemists Association
Mém. artillerie franç.	Mémorial de l'artillerie française (Paris)
Me". poudres	Mémorial des Poudres (Paris)
mg.	milligram(s)
min.	minimum
M. L. D.	minimum lethal dose
mm.	millimeter
mol.	molecular
m. q.	melting point
NG	nitroglycerine
OSM	Ordnance Safety Manual
P. A.	Picatinny Arsenal
PATR	Picatinny Arsenal Technical Report
pdr.	powder
powd.	powdered
p. p. m.	parts per million
press.	pressure
Proc. Roy. Soc.	Proceedings of the Royal Society (London)

psi	pounds per square inch
pt	part
Pyro	pyrotechnics
Rec. trav. chim.	Recueil des Travaux Chimiques des Pays-Bas (Dordrecht, Netherlands)
Rev.	revision
R. H.	relative humidity
rhomb.	rhombohedral
rhomb.	rhombic, orthorhombic
R. I.	report of investigation (followed by number)
R. T.	room temperature
satd. sol.	saturated solution (hygroscopicity determinations)
S	System (used with Ref. 44)
sl.	slightly
sol.	soluble
soly.	solubility
spec.	specification
sp. gr.	specific gravity
S. P. I.	Society of Plastic Industries
stat	static
S. T. P.	Standard Temperature and Pressure
sup	supplement
T	temperature
tech.	technical(ly)
temp.	temperature
TGA	thermogravimetric analysis
Trans. Faraday Soc.	Transactions of the Faraday Society (Aberdeen, Scotland)

T. P.	transition point
U. L.	Underwriters Laboratories, Inc. , Bulletin of Research
U. N.	United Nations
vac.	vacuum
vol. , V.	volume
wt.	weight
Zeit. anorg. Chem.	Zeitschrift fur anorganische und allgemeine Chemie
Z. Elektrochem.	Zeitschrift für Elektrochemie und angewandte physikalische Chemie (Berlin)
Zeit. Physik.	Zeitschrift fur Physik
Zhur. Fiz. Khim.	Zhurnal Fizicheskoi Khimii (Journal of Physical Chemistry, Moscow, U. S. S. R.)

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*This listing gives the main sources from which material has been collected. Numbers in the Ref. column on each data sheet are keyed to these general references.

References that pertain only to specific data sheets are listed at the end of the data sheets under Additional References. Numbers in the Ref. column preceded by Addnl. Ref. are keyed to those references. Some Additional References are sources from which no data were taken but which contain pertinent information on specific ingredients.

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ACETONE, (CH₃)₂CO
(Dimethyl Ketone, β-Ketopropane, 2-Propanone, Pyroacetic Ether)

Structural Formula :	$\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C} - \text{C} - \text{CH}_3 \end{array}$	
Specification No. :	JAN-A-489	
Molecular Weight :	58.08	
Crystalline Form :	liquid	
Color:	colorless	
Density, g./ml. :	(liquid) 0.792 at 4–20°C	
Coefficient of Thermal Expansion, cubical at 20°C:	1.487×10^{-3}	1
cubical at 0–54°C : $V_t = V_0 (1 + 1.3240t + 3.8090t^2 - 0.87983t^3)$		1
Heat of Formation, Kcal./mole at 298°K :	(liquid) -59,240	Addnl. Ref. 4
Free Energy of Formation, Kcal./mole at 298°K :	37,120	Addnl. Ref. 5
Entropy, cal./deg./mole at 298°K :	47.9	Addnl. Ref. 5
at B.P. (ideal gas) :	72.7	Addnl. Ref. 6
Melting Point :	177.5°K (-95.5°C)	1
Heat of Fusion, cal.(15°)/g. :	23.4	1
Boiling Point :	329.5°K (56.5°C)	1
Heat of Vaporization, cal./g. at 56.1°C :	124.5	1, 42
cal./mole :	6952 ± 1	Addnl. Ref. 7
Transition Point :	—	
Heat of Combustion, Kcal./mole at 20°C and 1 atm.:	426.8	1
Heat of Sublimation :	—	
Autoignition Temperature, in air :	700°C	71
	1118°F	75
Enthalpy Change of Enolization at 25°C :		Addnl. Ref. 2
Me ₂ CO (liquid) → CH ₂ = CMeOH (liquid) Kcal./mole :		7

HEAT CAPACITY OF ACETONE
Set I, Reverse-flow Calorimeter, 760 mm.

t, °C	61	75	90	105
T, °K	334	348	363	378
c _p , cal./g./deg.	0.375	0.374	0.380	0.384
C, cal./mole/deg.	21.8	21.7	22.1	22.3
t, °C	120	135	155	165
T, °K	393	408	428	438
c _p , cal./g./deg.	0.390	0.398	0.416	0.420
C _p , cal./mole/deg.	22.7	23.1	24.2	24.4

Addnl. Ref. 1

Acetone, (CH₃)₂CO (page 2)

Set II, Direct-flow Calorimeter, 760 mm.

t, °C	59.4	74.6	99.1	149.4
T, °K	332.6	347.8	372.3	422.6
c _p , cal./g./deg.	0.376	0.374	0.380	0.406
C _p , cal./mole/deg.	21.8	21.7	22.0	23.6

See also Addnl. Ref. 8

Decomposition Temperature and Products: Between 506° and 632°C, the products of decomposition are about 1/3 saturated hydrocarbons and hydrogen, 1/3 CO, and the remainder CO₂ and ethylene.

Vapor Pressure :

Press. "	1	10	40	100	400	760	M. P.
Temp. °C	-59.4	-31.1	-9.4	+7.7	39.5	56.5	-94.6

X-Ray Crystallographic Data :

Interatomic Distances and Molecular Configuration

C - C	1.57 ± 0.04A	< C - C - O	123°
C - O	1.14		Planar
C - H	1.09		

Hygroscopicity :

Solubility Data : Miscible in all proportions with water, alcohol, ether.
Soluble in chloroform.

Health Hazard : Prolonged or repeated inhalation or contact may have a variety of harmful effects although cases of serious poisoning are rare. Also has a narcotic effect, usually not chronic.

M.A.C. : 1000

Safety Classifications :

OSM : Class I, flammable liquid (flash point below 20°F)

ICC : Listed under "Explosives and Other Dangerous Articles" as a flammable liquid ; red label

Underwriters' Laboratory : 90 (gasoline class)

Fire and Explosion Hazard: Dangerous when exposed to flame. The vapors form an explosive mixture with air; explosive range (% acetone by volume) 2.55 to 12.8%. Can be ignited by an electric spark. Reacts vigorously with oxidizing materials. Forms an explosive mixture with high concentrations of hydrogen peroxide. To fight fire use water, carbon dioxide, dry chemical, or carbon tetrachloride. For precautions in storage, handling, and dispensing, see Refs. 26 and 14.

Caution: Keep away from fire.

Electrostatic Sensitivity : Readily ignited by static discharge.

Use in Pyrotechnics : as a solvent

Additional References :

- 1) "The Heat Capacity of Organic Vapors. VI. Acetone," B. Collins et al., J. Am. Chem. Soc. 72,2929 (1949)

52V1,
Addnl. Ref. 3

1

55, 85

1

12, 25, 29, 14

12, 25, 26, 14,
12V75

14

Acetone, $(\text{CH}_3)_2\text{CO}$ (page 3)

- 2) "The Heat of Hydrolysis of i-Propenyl Acetate and m-Cresyl Acetate and the Heat of Enolization of Acetone," S. Sunner, **Acta Chem. Scand.** **11**, 1757 (1957)
- 3) "Thermal Decomposition of Acetone in the Gaseous State," C. N. Hinshelwood and W. K. Hutchison, **Proc. Roy. Soc. A** **iii** 245 (1926). Abstracted in Br, Chem. Abstr.
- 4) "Free Energies of Some Organic Compounds," G. S. Parks and H. M. Hoffman, The Chemical Catalogue Co., New York (1932)
- 5) "The Heat Capacities of Isopropyl Alcohol and Acetone from 16° to 298°K and the Corresponding Entropies and Free Energies," K. K. Kelly, **J. Am. Chem. Soc.** **51**, 1145 (1929)
- 6) "The Entropy of Acetone and Isopropyl alcohol from Molecular Data. The Equilibrium in the Dehydrogenation of Isopropyl alcohol," S. C. Schumann and J. G. Aston, **J. Chem. Phys.** **6**, 485 (1938)
- 7) "The Thermodynamic Properties of Acetone," R. Pennington and K. A. Kobe, **J. Am. Chem. Soc.** **79**, 300 (1957)
- 8) "Estimation of the Heat Capacities of Organic Liquids," A. Johnson and Chen-Jung Huang, **Can. J. Technol.** **33**, 421 (1955)

ALCOHOL, C₂H₅OH
(Ethyl Alcohol, Ethanol, Methyl Carbinol,
Spirit of Wine, Grain Alcohol, Ethylic Alcohol,
Rectified spirit = 90-95% alcohol)

Refs.

Specification No. : **MIL-E-463A**
The specification covers grades **1, 2, 5, and 6**, of which only **grade 2** (min. **91.9%** alcohol by vol.) is used in pyrotechnics.

Molecular Weight : **46.07**
Crystalline Form : **liquid**
Color : **colorless**
Density, g./ml. : **(liquid) 0.7893**
Coefficient of Thermal Expansion, cubical at 20°C: **1.12 × 10⁻³**
V_t = V₀ (1 + 1.012 × 10⁻³ + 2.20 × 10⁻⁶) (for 99.374 by vol.)
Heat of Formation, Kcal./mole at 298°K **(gas) -56.24**
(liquid) -66.356

1
27
1, 41
9

See Table a
Free Energy of Formation, Kcal./mole at 293°K: **(gas) -40.30**
(liquid) -41.77

9

See Table a
Entropy, Kcal./mole : **(gas) 67.4**
(liquid) 38.4

9

See Table a
a. ENTROPY, FREE ENERGY, AND RELATED QUANTITIES
ETHYL ALCOHOL IN THE IDEAL GAS STATE AT
1-ATMOSPHERE PRESSURE
(E₀ = -52,260 cal./mole⁻¹)

Addnl. Ref. **5**

T	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$	S⁰	-F⁰	Δ F⁰ *	log₁₀ K *
°K	cal./deg. ¹ mole ¹	cal./deg. ¹ mole ¹	cal./mole⁻¹	cal./mole ¹	$-\frac{\Delta F^\circ}{R.T.}$ 2.3026
298.16	54.27	66.45	68,440	-40,010	29.329
300.00	54.34	66.56	68,560	-39,910	29.075
400	58.11	72.11	75,500	-34,310	18.749
500	61.42	77.12	82,970	-28,470	12.447
600	64.43	81.76	90,920	-22,490	8.191
700	67.22	86.08	93,310	-16,390	5.118
800	69.84	90.12	108,130	-10,230	2.796
900	72.31	93.92	117,330	-4030	0.980
1000	74.65	97.48	126,910	+2190	-0.479
1100	76.88	100.85	136,830	8430	-1.675
1200	79.02	104.04	147,080	14,680	-2.673
1300	81.07	107.06	157,650	20,920	-3.517
1400	83.02	109.94	168,500	27,170	-4.239
1500	84.92	112.67	179,640	33,410	-4.867

* Δ F⁰ and K are the free energy change and equilibrium constant, respectively, for the reaction forming ethyl alcohol from its elements in their standard states at T K.

Alcohol, C₂H₅OH (page 2)

Melting Point:	158.6°K (-114.5°C)	9
Heat of Fusion, Kcal./mole :	1.200	9
Boiling Point :	351.7°K (78.6°C)	9
Heat of Vaporization, Kcal./mole :	9.22	9
Transition Point:	—	
Heat of Sublimation :	—	
Heat Content or Enthalpy:		
See Table b		
Heat Capacity, cal./deg./mole at 298°K :	(liquid) 26.64	9
See also Addnl. Refs. 2 and 5 , and Table b		

**b. HEAT CAPACITY AT CONSTANT PRESSURE, HEAT CONTENT, AND
RELATED QUANTITIES OF ETHYL ALCOHOL IN THE
IDEAL GAS STATE
(EO = - 52,260 cal./mole⁻¹)**

Addnl. Ref. **5**

T	$\frac{H^\circ - E_g^\circ}{T}$	H°	$\Delta H^\circ *$	C_p°
°K	cal./deg. ¹ mole ⁻¹	cal./mole ⁻¹	cal./mole ⁻¹	cal./deg. ¹ mole ⁻¹
298.16	12.18	-48,630	-56,240	17.59
300.00	12.22	-48,600	-56,260	17.66
400	14.00	-46,660	-57,250	21.00
500	15.70	-44,410	-58,110	24.09
600	17.33	-41,860	-58,780	26.81
700	18.86	39,060	-59,320	29.18
800	20.28	-36,080	-59,710	31.25
900	21.61	-32,810	-60,000	33.07
1000	22.83	-29,430	-60,200	34.66'
1100	23.97	-25,900	-60,320	36.06
1200	25.02	-22,240	-60,370	37.28
1300	25.99	-18,470	-60,350	38.34
1400	26.91	-14,590	-60,250	39.27
1500	27.75	-10,630	-60,190	40.08

* ΔH° is the enthalpy of formation of ethyl alcohol from its elements in their standard **states** at the temperature T.

Decomposition Temperature :	—
Decomposition Products:'	burns to CO ₂ and H ₂ O

Alcohol, C₂H₅OH (page 3)

Vapor Pressure:

Press, mm.	1	10	40	100	400	760	M.P.
Temp. °C	-31.3	-2.3	+19.0	34.9	63.5	78.4	-112

X-Ray Crystallographic Data :

Hygroscopicity :

Solubility Data: Miscible with water and many organic solvents in all proportions.

Health Hazard : It is not considered an industrial poison, although large doses cause nausea, **vomiting**, impaired perception, lack of coordination, stupor, and even death. Habitual use may cause gastritis, delerium tremens, hallucinations, peptic ulcers, and hepatic cirrhosis.

Exposure to concentrations of 5000-10,000 ppm. irritates the eyes and mucous membrane;. Inhalation produces the same symptoms as ingestion.

M.A.C.: 1000

Safety Classifications :

OSM: Class I

ICC : Listed under "Explosives and Other Dangerous Articles." Flammable liquid - red label.

Fire and Explosion Hazard : Readily ignited by flame or static electric discharge.

Forms explosive mixture with air.

Explosive limits in air: 3.28 to 19% alcohol by vol.

Flash point : 55°F

Autoignition temperature : 799°F (95% alc.)
738°F (100% alc.)

For proper storage and handling see Refs.

Toright fire use CO₂, dry chemical, or CCl₄.

Electrostatic Sensitivity : Can be ignited by static electrical discharge.

Heat of Combustion, Kcal./mole at 20°C and 1 atm.:

327.6

Viscosity, centipoises at 20 °C (for abs. alcohol) :

1.22

Surface Tension, dynes/cm. at 20° C (for abs. alcohol) :

22.5

Use in Pyrotechnics:

for shellac solutions

See Spec. JAN-S-732

Additional References:

1) "Thermodynamic Properties of Ethyl Alcohol," R. C. Reid and J. M. Smith, Chem. Eng. Progr. 47, 415 (1951)

2) "Estimation of The Heat Capacities of Organic Liquids," A. Johnson and Chen-Jung Huang, Can. J. Technol. 33, 421 (1955)

Alcohol, C₂H₅OH (page 4)

- 3) "Heat Capacities of C₁₋₅ Aliphatic Alcohols," G. Simke and T. DeVries, J. Am. Chem. Soc. 75, 1815 (1953)
- 4) "Ethyl Alcohol," U. S. Industrial Chemical Co., Division of National Distillers and Chemical Corp., New York (1960)
- 5) F. Brickwedde et al., J. Research NBS 57, 270 (1946)
(thermodynamic data)
- 6) "The Technology of Solvents and Plasticizers," A. K. Doolittle, John Wiley & Sons, New York (1954)

ALUMINUM, Al (Aluminum)

Refs.

Specification No.: JAN-A-667

The specification covers **three** types, which **vary** in purity, and five **classes**, which vary in granulation and **apparent** density.

Type A—flat flakes manufactured **by** grinding or stamping.

Type B—granular or spheroidal **particles** manufactured by the atomizing process or **by** grinding.

Type C—granular or spheroidal **particles** manufactured by the atomizing **process**.

Molecular Weight: 26.98

1

-191 to + 16	18.35×10^{-6}	40	23.14×10^{-6}
20	25.5×10^{-6}	600	31.50×10^{-6}

1

5

5

5

5

5

5

5

5

5

4, 5

Aluminum, Al (page 2)

a. HEAT CONTENT AND ENTROPY OF Al (c, 1)

(Base, crystals at 298.15°K; atomic wt., 26.98)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	600	1.72	1500	10,830	13.59
500	1230	3.14	1600	11,530	14.04
600	1890	4.34	1700	12,230	14.46
700	2580	5.40	1800	12,930	14.86
800	3310	6.38	1900	13,630	15.24
900	4060	7.26	2000	14,330	15.60
932 (c) . . .	4280	7.50	2100	15,030	15.94
932 (l) . . .	6850	10.26	2200	15,730	16.27
1000	7330	10.75	2300	16,430	16.58
1100	8030	11.42	2400	17,130	16.88
1200	8730	12.03	2500	17,830	17.16
1300	9430	12.59	2600	18,530	17.44
1400	10,130	13.11	2700	19,230	17.70

Al (c) :

Enthalpy : $H_T - H_{298.15} = 4.94T + 1.48 \times 10^{-3}T^2 - 1604$ (0.6percent ; 298° - 932°K)

Heat Capacity : $C_p = 4.94 + 2.96 \times 10^{-3}T$; ΔH_{932} (fusion) = 2570

Al (l) :

Enthalpy : $H_T - H_{298.15} = 7.00 + 33G$ (0.1percent ; 932° - 2700°K)

b. HEAT CONTENT AND ENTROPY OF Al(g)
(Base, ideal gas at 298.15°K; atomic wt., 26.98)

4

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	515	1.49	1900	7995	9.27
500	1020	2.62	2000	8490	9.53
600	1520	3.53	2200	9485	10.00
700	2020	4.30	2400	10,480	10.43
800	2520	4.97	2600	11,470	10.83
900	3020	5.55	2800	12,470	11.20
1000	3515	6.08	3000	13,460	11.54
1100	4015	6.55	3500	15,950	12.31
1200	4515	6.99	4000	18,440	12.98
1300	5010	7.38	4500	20,950	13.57
1400	5510	7.75	5000	23,490	14.10
1500	6005	8.10	6000	28,790	15.07
1600	6505	8.42	7000	34,640	15.97
1700	7000	8.72	8000	41,440	16.87
1800	7500	9.00			

Al(g) :

Enthalpy : $H_T - H_{298.15} = 4.97T - 0.12 \times 10^{-5}T^2 - 1442$ (0.1 percent; 298° - 5000°K)Heat Capacity : $C_p = 4.97 + 0.12 \times 10^{-5}T^2$

c. HEAT CAPACITY OF ALUMINUM*

5

Solid from 298° to 932°K	
Liquid from 932° to 2720°K	
Gas from 2720° to 3000°K	
T, °K	C _p ^o (cal./deg./mole)
298	5.82
400	6.12
600	6.72
800	7.31
1000-2700	7.00
2800-3000	4.97

*See also C_p equations directly above

Decomposition Temperature : —

Decomposition Products : —

Vapor Pressure :

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	1284	1487	1635	1749	1947	2056	660

Aluminum, AP (page 4)

X-Ray Crystallographic Data :				1
<i>System</i>	<i>Space group</i>	<i>a</i>	<i>Molecules/Unit Cell</i>	
cubic	O_h^1	5.43 Å	4	
Hygroscopicity, cumulative increase in weight after :				51
		<i>Atomized</i>	<i>Stamped</i>	
Storage over H_2O for 29 days :		55.2%	0.6%	
Storage over H_2SO_4 for 29 days :		50.2%	0.0%	
Two days in oven at 105°C :		47.8%	-1.4%	
solubility Data : In alkali ; hydrochloric,				1
sulphuric acids :		soluble		
In nitric acid, acetic acid :		insoluble		
Health Hazard : None. Not usually considered an industrial poison. Aluminum dust can irritate the eyes. Inhalation of dust may cause chronic pulmonary disease.				12
M.A.C. :		50 million particles/ft. ³ (15mg./m. ³)		25
Safety Classifications:				
OSM : Class 1. Class 2 when not packed or stored in original shipping containers or equivalent (types I and II).				14
U.N. : Inflammable solid, which in contact with water emits flammable gas.				15
Fire and Explosion Hazard: Dust may ignite when exposed to heat of flame. May ignite by chemical action with oxidizers. Powder easily ignited or initiated to explosion by discharges of static electricity. See Electrostatic Sensitivity below.				12, 14, 49, 51
Caution: Keep water away. Evolution of hydrogen gas may result in explosion. When compounded with oxidizing agents, the powdered metal is a dangerous fire and explosion hazard. Special mixtures of dry chemicals should be used to fight aluminum fires.				
See also Ref. 86				
Electrostatic Sensitivity: Minimum energy required for ignition of powder by electric sparks (millijoules)				26
		<i>Dust Cloud</i>	<i>Dust Layer</i>	
Atomized :		15	2.5	
Stamped :		10	1.5	
Ignition Temp. of Al powders, °C :				26
		<i>Dust Cloud</i>	<i>Dust Layer</i>	
Atomized :		640	750	
Stamped :		550	470	
Minimum Explosive Concentration, mg./l. :				26
Atomized :		40		
Stamped :		35		
Used in Pyrotechnics : Aluminum is used as a fuel. It produces an intense white light on burning, but no distinctive flame coloration.				17, 20
Additional References:				
1) Ref. 64				

ALUMINUM OXIDE, Al_2O_3
(Alumina, α -Alumina, Corundum, Alundum)

Refs.

Percent Oxygen :	47.08
Specification No. :	MIL-A-10825
Molecular Weight :	101.96
Crystalline Form :	hexagonal
Color :	colorless
Density, g./ml. :	(solid) 3.99 (liquid) 2375-2625°K $5.632-1.127 \times 10^{-4}T$

1
1
31A
Addnl. Ref. 5

Alumina may exist in several forms at low temperature, but they are all converted to α -alumina (corundum) by heating above **1600°C**. The change is irreversible.

β -Alumina is an impure form that occurs from sodium or potassium aluminate.

<i>Form</i>	<i>Crystalline Structure</i>	<i>Density</i>	<i>Source</i>	<i>Temp. of Transformation to corundum, °C</i>
α	hexagonal	3.965		stable form
γ	spinel type	—	dehydration of γ (hydrous) Al_2O_3	> 1200
γ'	cubic	3.619	electrolytic oxidation of Al	750-1000
δ	hexagonal	2.40	dehydration of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	950
ϵ	cubic	—	electron diffraction	—
ζ	octahedron	3.6	from lithium melts	> 1600

Coefficient of Thermal Expansion, linear for alundum,

25°-900°C: **8.7×10^{-6}**

Heat of Formation, Kcal./mole : (corundum) α (c) 399.09
 γ (c) -384.84

See Table a

Free Energy of Formation, Kcal./mole at 298°K : (corundum) -376.77

See Table a

31
9
9

Aluminum Oxide, Al₂O₃ (page 2)

Heat and Free Energy of Formation:

a. HEAT AND FREE ENERGY OF FORMATION OF Al₂O₃ (CORUNDUM)

T, °K	Δ H (cal./mole)	Δ F° (cal./mole)
298.16	-399,600 (± 900)	-377,300 (± 900)
400	-399,700	-369,600
500	-399,600	-362,100
600	-399,500	-354,600
700	399,200	-347,100
800	-399,100	-339,700
900	-398,900	-332,300
931.7	398,800	-329,900
931.7	-403,900	-329,900
1000	-403,700	-324,600
1100	-403,400	-316,700
1200	-403,000	308,800
1300	-402,600	-300,900
1400	-402,300	-293,100
1500	-401,900	-285,400
1600	-401,500	-277,600
1700	-401,200	-269,900
1800	-400,800	-262,200
1900	-400,400	-254,500
2000	-400,100	-246,800

Phase Changes of Metal

M. P., 931.7°K ; Δ H = 2570 cal./g.-atom

Free Energy Equations:

Reaction	Range of Validity, °K
1) 2Al(c) + 3/2 O ₂ (g) = Al ₂ O ₃ (corundum)	298.16 to 931.7
Δ F° = -404,480 - 15.68T log T + 2.18 (10 ⁻³ T ²) + 3.935 (10 ⁵ T ⁻¹) + 123.64T	
2) 2Al(l) + 3/2 O ₂ (g) = Al ₂ O ₃ (corundum)	931.7 to 2000
Δ F° = -407,950 - 6.19T log T - 0.78 (10 ⁻³ T ²) + 3.935 (10 ⁵ T ⁻¹) + 102.37T	
Entropy at 298°K, cal./deg./mole (corundum) :	12.186
See Table b	
Melting Point :	2313°K (2040°C)
Heat of Fusion, Kcal./mole :	26.0
Boiling Point :	2523°K (2250°C)
corundum (α-alumina)	3773°K (3500°C)
Heat of Vaporization :	—

Aluminum Oxide, Al₂O₃ (page 3)

Transition Point: _____
 Heat of Transition: _____
 Heat of Sublimation: _____
 Heat Content or Enthalpy: _____

T, °K	H _T - H _{298.15}	S _T - S _{298.15}	T, °K	H _T - H _{298.15}	S _T - S _{298.15}
400	2150	6.17	1300	27,730	38.87
500	4580	11.59	1400	30,800	41.11
600	7200	16.36	1500	33,890	43.27
700	9960	20.61	1600	36,990	45.27
800	12,810	24.42	1700	40,100	47.16
900	15,720	27.84	1800	43,220	48.94
1000	18,670	30.95	1900	46,350	50.63
1100	21,660	33.80	2000	49,490	52.24
1200	24,680	36.43			

Al₂O₃ (c) :

Enthalpy: $H_T - H_{298.15} = 27.49T + 1.41 \times 10^{-3}T^2 + 8.38 \times 10^5T^{-1} - 11,132$
 (0.5 percent; 298° - 1800°K)

Heat Capacity: $C_p = 27.49 + 2.82 \times 10^{-3}T - 8.38 \times 10^5T^{-2}$

Heat Capacity, cal./deg./mole : (solid) 18.88 **4, 9**

See Table b for equation

Decomposition Temperature : 3800°K ± 200 **8**

Decomposition Products: 2AlO (gas) + O **63**

For DTA see Addnl. Ref. 4

Vapor Pressure :

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	2148	2385	2549	2665	2874	2977	2040

X-Ray Crystallographic Data (α-corundum) :

<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>c</i>	<i>Molecules/Unit Cell</i>	
hexagonal	D _{3d} ⁶	5.56Å	22.55Å	2	1

Hygroscopicity : Powdered Al₂O₃ readily absorbs moisture from the air. **29**

Solubility Data :

In water at 29°C:	0.000098 g./100 g.	1
In hot water:	insoluble	
In acids and alkalies:	very slightly soluble	

Aluminum Oxide, Al_2O_3 : page 4)

Health Hazard: High concentrations of dust may be irritating to the respiratory tract and cause Shaver's disease, **29**

M.A.C. : 50 million particles/ft.³ **12**

Safety Classifications : _____

Fire and Explosion Hazard: _____

Electrostatic Sensitivity: _____

Use in Pyrotechnics: A small amount of alumina added to powdered red phosphorus maintains it in a free flowing condition and free from lumps.

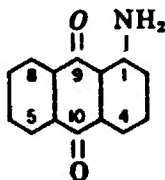
**Spec. MIL
10825**

Aluminum oxide is formed when aluminum or any of its compounds are burned in air, or in a sufficient amount of oxidizer or oxygen.

Additional References :

- 1) A. D. Mah, J. Phys. Chem. **62, 572 (1957)** (gives the value for Heat of Formation as $-400.48 \pm .25$ Kcal./mole)
- 2) "The Gaseous Species of the Al- Al_2O_3 System," L. Brewer and A. Searcy, J. Am. Chem. Soc. **73, 5308 (1951)** . (disassociation pressures)
- 3) Ref. 64
- 4) "Differential Thermal Analysis of Organic Compounds," A. T. Perkins and H. L. Mitchell, Trans. Kansas Acad. Sci. **60, 437 (1957)**
- 5) "The Density of Liquid Aluminum Oxide," A. D. Kirshenbaum and J. A. Cahill, J. Inorg. Nucl. Chem. **14, 283 (1960)**

1-AMINOANTHRAQUINONE, C₁₄H₉NO₂
(1-Amino-9,10-Dihydro-9,10-Dioxoanthracene ;
Fast Red Al; α -Anthraquinonylamine, C.I. 37275, Azoic Component 36)



Structural Formula :

Specification No. :

Molecular Weight :

Crystalline Form :

Color :

Density :

Coefficient of Thermal Expansion :

Heat of Formation:

Free Energy of Formation:

Entropy :

Melting Point :

Heat of Fusion:

Boiling Point :

Heat of Vaporization, Kcal./mole at **298°K**
and 1 atm.:

Transition Point:

Heat of Sublimation :

Heat Content or Enthalpy:

Heat Capacity :

Decomposition Temperature :

For DTA and **TGA** see Ref. 81

Decomposition Products :

Vapor Pressure :

X-Ray Crystallographic Data :

For absorption spectra see Ref. 66

Hygroscopicity :

Solubility Data :

In water, g./100 g. at **25°C** :

at **80°C** :

In ether, chloroform, benzene :

In glacial acetic acid, **11. at 11.5°C** :

MIL-D-3698

223.23

needles

red

—

—

—

—

—

525°K (252°C)

526°K (253°C)

—

sublimes

28.7 ± 0.1

—

—

—

—

—

—

—

—

—

—

—

—

0.00004

0.0009

soluble

dissolves 3.3 g.

Refs.

1, 84, 48A

88V14

1
84

1, 88V14

Addnl. Ref. 1

Addnl. Ref. 2
1, 28, 88V14
and **V17**

1-Aminoanthraquinone, $C_{14}H_9NO_2$ (page 2)

In 92-96% H_2SO_4 :	dissolves with yellow color
In oleum, 20% SO_3 :	dissolves with red color
In concentrated HCl :	dissolves
Health Hazard :	_____
Safety Classifications :	
OSM :	not listed
ICC :	not listed
Fire and Explosion Hazard:	_____
Electrostatic Sensitivity :	_____
Use in Pyrotechnics: Tb color smoke mixtures red. Used in orange smoke mixtures.	

Additional References :

- 1) "A Radioactive Ionization Gauge and its Application to the Measurement of Latent Heat of Vaporization," J. H. Beynon and G. R. Nicholson, J. Sci. Instr. **53**, 376 (1956)
- 2) J. Soc. Dyers Colourists **70**, 68-77 (1954)

AMMONIUM NITRATE, NH_4NO_3							Refs.	
Percent Oxygen :		60						
Specification No. :		JAN-A-175						
. The specification covers grade I and grade II, which differ slightly in purity. Grade I has three classes differing in granulation.								
Molecular Weight :		80.05						
Crystalline Form: Five forms as follows:								
Designation		System			Range °C			
I (ϵ)		regular (cubic) (isometric)			125.2 to 169.6			
II (δ)		rhombohedral or tetragonal			84.2 to 125.2			
III (γ)		orthorhombic			32.1 to 84.2			
IV (β)		orthorhombic			-16 to 32.1			
V (α)		tetragonal			-18 to -16			
Color:		colorless						
Density, g./ml. :		(solid) 1.725 at 25°C					1, 43	
		1.594 at 180 ± 5°C						
		δ 1.666 at 93 ± 5°C						
		γ 1.661 at 40 ± 1°C						
		β 1.725 at +25°C						
		α 1.710 at -25 ± 5°C						
Coefficient of Thermal Expansion:								
Coeff. $\times 10^6$		677	852	920	982	1069	1113	44
Temp. °C		-60	-20	0	20	60	100	
Heat of Formation, Kcal./mole at 298°K:		(c) -87.27					9	
		-87.93					1A	
Free Energy of Formation, Kcal./mole at 298°K :		(c) -43.82					Addnl. Ref. 11	
Entropy, cal./deg./mole at 25°C :		36.0					Addnl. Ref. 11	
See Table a								
Melting Point :		442.8°K (169.7°C)					9	
Heat of Fusion, Kcal./mole :		1.3					9	
		1.53					Addnl. Ref. 9	
Boiling Point :		decomposes at 483°K (210°C)					1	
Heat of Sublimation :		—						

a. HEAT CONTENT AND ENTROPY OF NH_4NO_3 (c, 1)
(Base, α -crystals at 298.15°K)

4

$T, ^\circ\text{K}$	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	$T, ^\circ\text{K}$	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
305.3 (α) . . .	240	0.80	398.4 (δ) . . .	4830	13.66
305.3 (β) . . .	620	2.04	400	4900	13.83
325	1180	3.82	425	6040	16.60
350	1890	5.92	442.8 (δ) . . .	6860	18.48
357.4 (β) . . .	2100	6.52	442.8 (l) . . .	8160	21.42
357.4 (γ) . . .	2420	7.41	450	8440	22.05
375	3020	9.05	500	10,360	26.09
398.4 (γ) . . .	3820	11.12	550	12,290	29.77

 $\text{NH}_4\text{NO}_3(\alpha)$:Enthalpy : $H_T - H_{298.15} = 33.601' - 10,018$ (0.1 percent ; 298° - 305.3°K)Heat Capacity : $C_p = 33.60$; $A_{305.3}$ (transition) = 380 $\text{NH}_4\text{NO}_3(\beta)$:Enthalpy : $H_T - H_{298.15} = 28.40 - 8051$ (0.1 percent ; 305.3° - 357.4°K)Heat Capacity : $C_p = 28.40$; $A_{357.4}$ (transition) = 320 $\text{NH}_4\text{NO}_3(\gamma)$:Enthalpy : $H_T - H_{298.15} = 34.10T - 9767$ (0.1 percent ; 357.4° - 398.4°K)Heat Capacity : $C_p = 34.10$; $A_{398.4}$ (transition) = 1010 $\text{NH}_4\text{NO}_3(\delta)$:Enthalpy : $H_T - H_{298.15} = 45.601' - 13,337$ (0.1 percent ; 398.4° - 442.8°K)Heat Capacity : $C_p = 45.60$ $\text{NH}_4\text{NO}_3(l)$:Enthalpy : $H_T - H_{298.15} = 38.501' - 8887$ (0.1 percent ; 442.8° - 550°K)Heat Capacity : $C_p = 38.50$

Decomposition Temperature, °C : 210

Decomposition Products: These vary with the conditions of decomposition or explosion. Many different equations for the decomposition reactions are given in the literature. Practically all involve oxides of nitrogen.

For DTA see Refs. 33, 47, and Addnl. Ref. 10

Dissociation Pressure :

Press. mm. Hg.	3.25	7.46	11.55	15.80	27.0	41.0	M.P.
Temp. °C	188	205	216	223	237	249	169.6

See also Addnl. Ref. 3

1, 13
43

Addnl. Ref. 11

Ammonium Nitrate, NH₄NO₃ (page 3)

b. X-RAY CRYSTALLOGRAPHIC DATA

<i>Designation</i>	<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>Molecules/ Unit Cell</i>
ε or I	cubic		4.40			1
δ or II	tetragonal		5.75		5.00	2
γ or III	orthorhombic	V _h ¹⁶	7.06	7.66	5.80	4
β or IV	orthorhombic	V _h ¹³	5.75	5.45	4.96	2
α or V	rhombic	V _h ¹³	4.928	5.434	5.732	2

1

R.H.%	31	43	52	65
	24 hrs. Equil.	24 hrs. Equil.	24 hrs. Equil.	24 hrs. Equil.
Gain mg./g.	0.3 0.5	0.3 0.5	0.7 1.0	131.6 —

32

Addnl. Ref. 7

13

Water		Alcohol		Nitric Acid			Pyridine		Acetic Acid	
°C	%	°C	%	°C	%	% HNO ₃	°C	%	°C	%
0	118			0	45.1	30.0	25	Approx.	16.6	0.0
20	192	20	2.5	15	73.0	21.7	20-25		27.0	0.39
40	297	40	5	30	106	20.8			80.9	5.8
60	421	60	7.5	75	201	31.6			101.0	20.7
80	580	78	10.5						120.0	125
100	871									

Solubility, g./100 solvent :

In ethyl alcohol at 20°C :

3.8

In methyl alcohol at 20°C :

17.1

In acetone and NH₃ :

slightly soluble

29

Health Hazard : Average or large doses may cause nausea and vomiting. Moderately toxic on ingestion or inhalation.

29, 98

Safety Classifications :

OSM : Class 12. "When stored in an area where explosives may be projected into the nitrates, the regulations for Class 9 are applicable. When stored in an area with fire hazards only and separated by inhabited building distances from areas containing ammunition, ammonium nitrate may be stored in accordance with the regulations governing the storage of Class 2 solid propellants."

ICC : Oxidizing material ; yellow label.

Ammonium Nitrate, NH_4NO_3 , (page 4)

Fire and Explosion Hazard : Many disastrous explosions have been attributed to ammonium nitrate. Although it is relatively insensitive as a high explosive by itself, if allowed to burn unconfined, its tendency to explode increases with pressure and the presence of oxidizable materials. Contamination with chlorides, nitrocompounds, sulfur, charcoal, metallic nitrates, metal powders, petroleum derivatives and oxidizable carbonaceous materials sensitizes ammonium nitrate, accelerates its decomposition and increases the violence of the reaction. Zinc or lead contamination lowers the decomposition temperature to below 100°C . Galvanized metals and lead solder should, therefore, not be used in the vicinity of ammonium nitrate. Fires involving ammonium nitrate should be vented to the greatest possible extent because air acts as a diluent for the hazardous gases, minimizing the probability of explosion. Fires should be fought with large quantities of water but never with steam.

See also Addnl. Ref. 12

Electrostatic Sensitivity:

Heat of Combustion, Kcal./mole :

$Q_c = 50.3$

Addnl. Ref. 8

$Q_p = 49.4$

Heat of Explosion, cal./g.:

346

13

gas volume, cc./g. :

980

Heat and Stability Tests:

75°C International Heat Test, % loss in 48 hours:

0.0

13

100°C Heat Test:

% loss first 48 hrs.:

0.74

13

% loss second 48 hrs.:

0.13

explosion in 100 hrs.:

none

Vacuum Stability Tests, gas evolved in 40 hrs.

at 100° , 120° , and 150°C :

0.3 cc.

13

Explosion Temperature Test, 5 sec. point, $^\circ\text{C}$:

ignites at 465

13

Rifle Bullet Impact Test (at density of 1.2 g./ml.) :

unaffected in 100 trials

13

Sensitivity to Initiation, g. teteryl needed to initiate :

0.25

13

Trauzl Test, % TNT:

56

13

Friction Sensitivity :

unaffected by steel shoe

13

Impact Sensitivity : Effect of temperature on ground, C.P. Ammonium Nitrate.

13

Temp. $^\circ\text{C}$	P.A. Impact Test with 2 kg. weight, in.	(10% point)
25	31	
75	28	
100	27	
150	27	
175	12	

Ammonium Nitrate, NH_4NO_3 (page 5)

13

Specific Heat: at °C	-150	-100	-50	0	50	100
cal./g./°C	0.189	0.330	0.364	0.397	0.414	0.428

Compatibility with Metals: In the presence of moisture, ammonium nitrate reacts with copper, iron, steel, brass, lead, and cadmium. See Addnl. Ref. 1

Uses in Pyrotechnics: as an oxidizing agent

Additional References :

- 1) "Military Explosives," **TM-9-T011A-1-34**, Departments of the **Army** and the Air Force **(1955)**
- 2) "Investigation of Sensitivity of Fertilizer Grade Ammonium Nitrate to Explosion," P. Macy et al., PATR-1658, Picatinny Arsenal, Dover, **N.J.** **(1947)**
- 3) "The Dissociation Pressure and Free Energy of Formation of Ammonium Nitrate," A. D. Little, Inc., **J. Am. Chem. Soc.** **76**, **(1954)**
- 4) "On the Thermogravimetry of Analytical Precipitates," C. Duval and N. Xuong, **Anal. Chem. Acta** **6**, **246** **(1952)**
- 5) DTA and TCA, **Ref. 33**
- 6) **Ref. 54V2**, general reference
- 7) "Hygroscopic Properties of Sodium, Potassium and Ammonium Nitrates, Potassium Chlorate and Mercury Fulminate," G. B. Taylor and W. C. Cope, **Met. and Chem. Eng.** **15**, **141** **(1916)**
- 8) L. Médard and M. Thomas, **Mém. poudres**, **35**, **155, 160 and 172** **(1953)**
- 9) "The Cryoscopic Heat of Fusion of Ammonium Nitrate," A. G. Keenan, **J. Phys. Chem.** **60**, **1356** **(1952)**
- 10) "Differential Thermal Analysis of the Thermal Decomposition of Ammonium Nitrate," A. G. Keenan, **J. Am. Chem. Soc.** **77**, **1379** **(1955)**
- 11) "The Dissociation Pressure and Free Energy of Formation of Ammonium Nitrate," G. Feick, **J. Am. Chem. Soc.** **76**, **5858** **(1954)**
- 12) "Investigations on the Explosibility of Ammonium Nitrate," J. J. Burns et al., **Bur. of Mines, RI** **4994** **(1952)**
- 13) "The Thermal Decomposition of Ammonium Nitrate. Steady State Reaction Temperatures and Reaction Rate," G. Feick and R.M. Hainer, **J. Am. Chem. Soc.** **76**, **5860** **(1954)**

AMMONIUM PERCHLORATE, NH₄ClO₄

Refs.

Percent Oxygen :	54.47	
Specification No.:	JAN-A-1%	
The specification covers two grades which differ in purity and two classes which differ in granulation: grade 1 is used in tracers; grade 2 is used in HC Smoke Mixtures.		
Molecular Weight :	117.50	1
Crystalline Form :	rhambic	1
Color :	colorless	1
Density, g./ml. :	(solid) 1.95	1
Coefficient of Thermal Expansion (cubical) :	$\beta = (1/v) dV/dt$	Addnl. Ref. 4
Temp. °F	-25 0 25 50 75 100 125 150 175	
$\beta \times 10^4 / ^\circ F$	1.690 1.613 1.538 1.463 1.389 1.316 1.244 1.172 1.101	
Heat of Formation, Kcal./mole at 298°K :	-69.42	9
Free Energy of Formation, cal./g. at 298°K :	-665	13
	Kcal./mole : -78.14	
Entropy :	—	
Melting Point :	decomposes above 423°K (150°C)	20V3
Heat of Fusion :	decomposes before fusion	
Boiling Point :	decomposes	
Transition Point :	rhombic to cubic 513°K (240°C)	9
Ref. 72 cites α to β at 284°C and β to γ at 360°C.		
See also Ref. 47		
Heat of Sublimation :	—	
Heat Content or Enthalpy :	—	
Heat Capacity :	—	
Decomposition Temperature and Products :	Decomposes at a maintained temperature at 150°C. Decomposition products are NO ₂ and ClO ₂ .	14
Decomposition begins at 130°C, becoming explosive at 380°C. The decomposition varies with the temperature. Below 300°C, decomposition is mainly according to the equation :	65, Addnl. Refs. 5, 6, 7	
$4NH_4ClO_4 \rightarrow 2Cl_2 + 3O_2 + 8H_2O + 2N_2O$		
Above 350° the proportion of nitric oxide increases and becomes appreciable. Above 350° the following equation represents decomposition :		
$10NH_4ClO_4 \rightarrow 2\frac{1}{2} Cl_2 + 2N_2O + 2\frac{1}{2} NOCl + HClO_4 + 1\frac{1}{2} HCl + 18\frac{3}{4} H_2O + 1\frac{1}{4} N_2 + 68/02$		
The activation energy for decomposition varies with temperature. The following are several values for activation energy : 29.6 Kcal./mole below 240°C and 18.9 Kcal./mole above 240°C. Between 400° and 440°C the value is 73.4 Kcal./mole.		
For DTA see Ref. 47		
cited by Ref. 72		
47		

Ammonium Perchlorate, NH_4ClO_4 (page 2)

Vapor Pressure : _____

X-Ray Crystallographic Data :

System	Space Group	a	b	c	Molecules/Unit Cell
rhombic	V_h^{16}	9.202	5.816	7.447	4
		9.13	5.17	7.47	4
	D_{2h}^{18}	9.231	5.813	7.453	4

1
Addnl. Ref. 8
97V7

Hygroscopicity : Gain, in mg./g. of a purified sample at equilibrium at 70°F , after equilibrium had been established in a vacuum desiccator:

R.H. %	65	75	86	93
Gain mg./g.	0.5	0.5	0.4	0.8

32

Critical R.H.: 87.0% at 25°C

Solubility: In water, g./100 cc. of saturated solution:

13

Temp. $^\circ\text{C}$	0	25	60	100
Sol.	12	20	39	88

Solubility in Nonaqueous Solvents at 25°C :

65, 77

Solvent	g./100 g. solvent
acetone	2.26
ethyl acetate	0.032
ethyl alcohol	1.908
ethyl ether	insol.
methyl alcohol	6.85

Health Hazard : Moderate. Irritating to skin and mucous membranes.

12, 65

Evolves highly toxic fumes when heated to decomposition.

Moderately toxic on ingestion or inhalation.

Weak muscular poison; may cause convulsions. Harmful to thyroid.

93, 72

Safety Classifications :

OSM : **Class I**. **Class II** when not packed in original containers or equivalent.

ICC : Oxidizing material ; yellow label. Listed under "Explosives and Other Dangerous Articles."

Fire and Explosion Hazard : A powerful oxidizer, explodes violently when heated with sulphur, organic matter, or finely divided metals, particularly magnesium and aluminum. Exploded by shock. Fires involving ammonium perchlorate alone may be fought with water.

12, 14

Electrostatic Sensitivity : _____

Specific Volume : $V_t = a + bt + ct^2$

Addnl. Ref. 4

where $a = 0.5074 \text{ cm.}^3/\text{g.}$

$b = 0.819 \times 10^{-4} \text{ cm.}^3/\text{g.}/^\circ\text{F}$

$c = 0.704 \times 10^{-7} \text{ cm.}^3/\text{g.}/(^\circ\text{F})^2$

Ammonium Perchlorate, NH_4ClO_4 , (page 3)

Explosive Data :

Sensitivity: Requires the equivalent of **10 mg.** of mercury fulminate or an XC-32. Very insensitive **as** an explosive but more sensitive than Na, K, and Mg perchlorates. Drop test—min. : **86 in.** for **an 11-lb. wt.** Insensitive to severe friction. Heating small quantities **does** not result in an explosion. The temperature developed on explosion is **1308°C** and the heat liberated, 344.5 cal./g.

Brisance: Trauzl lead block test, expansion in cc. : **140.2**, equivalent to one-quarter that of 40% N.G. dynamite.

Velocity of Detonation, in **60 mm.** diameter iron tube and detonated with five No. 8 caps : **3800 m./sec.**

100°C Heat Test		Vacuum Stability Test		
loss first 48 hrs. %	0.02	cc. of gas evolved from 5 g. in 40 hrs. at		
loss second 48 hrs. %	0.00	100°C	0.13	
explosion in 100 hrs.	none	120°C	0.20	
		150°C	0.32	

200-Gram Bomb Wand Test, g. sand crushed: **6.0** 13

Sensitivity to Initiation : requires **0.25 grams** of tetryl 13

Explosion Temp. in 5 sec., °C: **435** 13

Temperature of Explosion, °C : (est.) **1084** 72

Impact Sensitivity, 2-kg. weight: 13

Bureau of Mines app., cm. (10% point) : **67**

Picatinny Arsenal app., in. (10% point) : **24**

Sample weight, mg. : **24**

Sensitivity to Friction : Bureau of Mines app., steel shoe; 100 trials—no explosion or ignition, one snap. 72

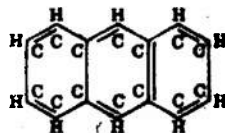
Use in Pyrotechnics : as an oxidizing agent

Additional References:

- 1) "The Use of Differential Thermal Analysis for Investigating the Effects of High Energy Radiation on Crystalline Ammonium Perchlorate," E. Freeman and D. Anderson, **J. Phys. Chem.** **63**,1344 (1959)
- 2) "Apparatus for Observing Physical Changes at Elevated Temperatures," V. Hogan and S. Gordon, **Anal. Chem.** **32**, 573 (1960)
- 3) "The Thermal Decomposition of Ammonium Perchlorate," L. Bircumshaw and B. Newman, **Proc. Roy. Soc. A** **227**, 115 (1954) ; also **A227**, 228 (1955)
- 4) Report **Q PR No. 492**, Aerojet General Corporation, Sacramento, Calif.
- 5) L. L. Bircumshaw and T. R. Phillips, **J. Chem. Soc.** 2957,4741 (1957)
- 6) "The Crystal Structure of Ammonium Perchlorate- NH_4ClO_4 ," K. Venkatesan, **Proc. Indian Acad. Sci.** **46A**, 134 (1957)

ANTHRACENE, $C_{14}H_{10}$ ($(CH_2)_2$), $C_{14}H_{10}$
(Green oil, P-Naphthalene)

Structural Formula:



Specification No.

JAN-A-202

The specification covers a technical grade in two classes, a and b, which differ in granulation.

Molecular Weight:

178.22

Crystalline Form:

monoclinic

Color:

colorless with violet fluorescence

Density, g./ml.:

(solid) 1.26

Coefficient of Thermal Expansion, cubical,
over the range 20–180°C:

$$V_{t_2} = V_{t_1} [1 + \alpha (t_2 - t_1) + \beta (t_2 - t_1)^2]$$

where $\alpha = 213 \times 10^{-6}$ and $\beta = 3.10 \times 10^{-7}$

Heat of Formation, Kcal./mole at 25°C at constant pressure:

26.53

Free Energy of Formation:

—

Entropy, cal./deg./mole at 298.1°K:

49.6

Melting Point:

490°K (217°C)

Heat of Fusion, cal. (15°/g.) at 216.55°C:

38.7

Boiling Point:

627°K (354–5°C)
339.9°C

Heat of Vaporization, Kcal./mole:

13.10

Transition Point:

—

Heat of Sublimation:

—

Heat Content or Enthalpy:

—

Heat Capacity:

—

Specific Heat:

Temp. °K	94.4	124.8	193.2	254.4	297.2	20–100	20–210	liquid
cal./g.	0.95	0.117	0.177	0.238	0.278	0.312	0.3688	0.509

Decomposition Temperature:

—

Decomposition Products:

—

Vapor Pressure:

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	145.0	187.2	217.5	250.0	310.2	342	217.6

Refs.

1, 12

1

29

1

Addnl. Ref. 4

Addnl. Refs.
1, 2

1

1

1

31A

57V13

57V13

1

Anthracene, C₆H₄(CH₂)₂C₆H₄ (page 2)

X-Ray Crystallographic Data :

<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>Axial Angle</i>	<i>Molecules/ Unit Cell</i>	
monoclinic	C _{2h}	8.58	6.02	11.18	β = 125°	2	57, 85
		8,561	6.036	11.163	β = 124°42'	2	
Hygroscopicity :							
Solubility Data, g./100 ml. In water:					very slight		1
In alcohol at 160°C:					insoluble		
at 78°C:					0.076		
In ether:					0.83		
In CHCl ₃ :					1.189		
In CS ₂ :					1.767		
In benzene at 80°C:					1.500		
					7.5		
Health Hazard: Purified white material is considered non-toxic. However, the impure technical product may be carcinogenic because of impurities present. Avoid repeated contact or inhalation of dusts or vapors. As a chronic local irritant it is considered severely toxic.							12, 25, 93
Fire and Explosion Hazard: Burns when heated in air. Vapors may explode when ignited in air. Gives off acrid fumes. Reacts with oxidizing materials. To fight fire, use water, foam, CO₂, dry chemicals, or CCl₄.							12, 26, 29, 67
Safety Classifications:							
OSM :					not listed		
ICC :					not listed		
Electrostatic Sensitivity : Anthracene dust clouds can be ignited and exploded by an electric spark.							Addnl. Ref. 3
Anthracene darkens on exposure to light.							29
Heat of Combustion, Kcal./mole at 20°C :					1700.4		1
Flash Point, °F (dosed cup) :					250		75
(open cup) :					385		
Autoignition Temperature, °F :					881		26, 75
Ref. 71 gives 472°C in air							
Explosive Limits in Air, % by vol., lower:					0.63		67
Use in Pyrotechnics :					as a fuel		
Additional References:							
1) J. Am. Chem. Soc. 68,2527 (1946)							
2) J. Am. Chem. Soc. 74,1451 (1952)							
3) A, Van Dussen, Rec. trav. chim. 54,873 (1935)							
4) W, Klem et al., Zeit. anorg. Chem. 176,10 (1928)							

ANTIMONY SULFIDE (tri), Sb ₂ S ₃						Refs.
(Antimony Trisulfide, Antimony Black, Black Antimony, Stibnite, Antimonite, ~~Needle~~ Antimony, Sulfur Gold, Sulfuret of Antimony, Antimony Glance)						
Specification No. :	MILA-159					
Molecular Weight :	339.72					
Crystalline Form :	rhombic					
Color :	black or red					
For color changes see Ref. 54V9						
Density, g./ml. :	(solid) 4.64					1
Coefficient of Thermal Expansion :	---					
Heat of Formation, Kcal./mole at 25°C :	(c) black, -43.5					1
	(amor.) orange, -36.0					1
Free Energy of Formation, Kcal./mole at 300°K (27°C) :	-66.0					40V2
Entropy, cal./deg./mole at 298.16°K :	(c) 39.6					3
	(c) 30.3 ± 4.0					24
Melting Point :	823°K (550°C)					1
Sinters in air at 440°C, melts at 510°C						54V9
Heat of Fusion, 15° cal./g. at 540°C :	17.6					1
Boiling Point : Volatizes above its melting temperature and <i>can</i> be distilled without decomposition						20V3
Heat of Vaporization :	---					54V9
Transition Point: See Ref. 54V9						
Heat of Transition, Kcal./mole :	violet to black, 4.3					54V9
	orange-red to black, 5.6					
Heat of Sublimation, Kcal./mole at M.P. :	51.2					24, 40V2
Sublimation Temperature, °C :	380					54V9
Heat Content or Enthalpy:	---					
Heat Capacity, cal./deg./mole at 298-821°K :	C _p = 24.2 + 13.2T					24
Decomposition Temperature: When heated in air, above 176°C, it is slowly converted to the oxide.	---					45
Decomposition Products :	loses S ; takes up O					
Vapor Pressure:						
	Press. mm.	about 0.033	1.17	13.45	244	44V18B
	Temp. °C	400	500	650	850	
X-Ray Crystallographic Data :						
System	Space Group	a	b	c	Molecules/Unit Cell	
rhombic	V _h ¹⁶	11.39	11.48	3.89	4	1
orthorhombic	V _{2h} ¹⁶	11.23	11.31	3.84	4	97V5

Antimony Sulfide (tai) , Sb_2S_3 (page 2)

Solubility Data :

In water at 18°C:	0.175×10^{-6} g./ml.
In hot water:	decomposes
In alk., NH_4HS , K_2S , HCl :	soluble
in acetic acid:	insoluble

Health Hazard : Irritates the skin and mucous membranes. May cause gastrointestinal upsets. A poison with symptoms similar to arsenic. A cardiac and nervous depressant. Antimony poisoning is detectable in the blood and by liver functioning.

M.A.C. :

0.5

Safety Classification :

OSM: Inert and presents no particular Are or toxic hazard as used in Ordnance establishments.

See also Addnl. Refs. 1 and 2

Fire and Explosion Hazard: Dangerous; when heated to decomposition or on contact with acid or acid fumes, it emits highly toxic fumes of oxides of S and Sb. It reacts with steam or water and produces toxic and inflammable vapors. Reacts vigorously with oxidizing materials such as chlorates or perchlorates.

Electrostatic Sensitivity :

Use in Pyrotechnics: Antimony sulfide is used as a fuel. It imparts a pale green color to burning compositions.

Additional References :

- 1) C.A. 42, 1711 (1948)
- 2) C.A. 65, 9748 (1951)

ASPHALTUM

(Gilsonite, Asphalt, Asphaltite, Earth Pitch,
Uintate or Uintahite, Mineral Rubber)

Specification No.:	JAN-A-356	17V2
Molecular Weight:	variable mined material, about 4250	Addnl Ref. 1
Crystalline Form:	amorphous	Addnl. Ref. 1
Color:	brown to black, leaves brown streak	Addnl. Ref. 1
Density, g./ml.:	(solid) 1.05-1.10	
Coefficient of Thermal Expansion, cubical:	$5-7 \times 10^{-4}$	
Heat of Formation:	—	
Free Energy of Formation:	—	
Entropy:	—	
Softening Point, specification min.:	398°K (125°C)	
Heat of Fusion:	—	
Boiling Point:	< 743°K (470°C)	12
Transition Point:	—	
Heat of Sublimation:	—	
Heat Content or Enthalpy:	—	
Heat Capacity:	—	
Decomposition Temperature and Products:	May be distilled to about 550°F	Addnl. Ref. 1
Above this temperature an exothermic reaction takes place with the rapid evolution of gaseous products. Between 475° and 650°F an oily distillate is obtained.		
Vapor Pressure:	—	
X-Ray Crystallographic Data:	—	
Hygroscopicity:	nonhygroscopic	
Solubility Data:	Insoluble in water, alcohol, acids, and alkalies. Soluble in petroleum, ether, and acetone. The specification requires the following CCl ₄ —99% min., petroleum ether—30% min., and CS ₂ —99% min.	29
Health Hazard:	Fumes or dust may irritate the eyes and respiratory tract. Moderately toxic, acute or chronic irritant.	29, 93
Safety Classifications:		
OSM:	not listed	
ICC:	not listed	
Fire and Explosion Hazard:	slight	75
Flash Point (closed cup) °F:	400	
(open cup) °F:	535	
Autoignition Temperature:	905	
To fight fire use foam, CO ₂ , dry chemical or CCl ₄		

Asphaltum (page 2)

Electrostatic Sensitivity :

Asphaltum is **formed from** petroleum as the result of heat and pressure working over geologic time. The type of **asphalt called** for in the specification is known as gilsonite or uintate and is found mainly in **Utah** and Colorado. Chemically, gilsonite consists mainly of **saturated** hydrocarbons substantially free from oxygenated bodies with little or no crystallizable paraffins. Gilsonite is marketed in **two grades known as "selects" or "firsts" and "seconds."** The "firsts" are from the center of the vein and have a lustrous conchoidal fracture. The "seconds" are **from near the walls** of the vein and **show a semiconchoidal and semilustrous fracture.** They are differentiated on the basis of softening point and behavior in petroleum solvents. Although gilsonite is a mined product it **shows** fairly uniform characteristics as follows:

Fracture :	conchoidal
Luster:	bright to fairly bright
Hardness on Moh's scale:	2
Fusing point, Kramer and Sarnow Method, °F:	230-350
Ball and Ring Method, °F:	270-400
Volatile in 5 hrs. at 325°F, %:	not less than 2
400°F, %:	not less than 4
500°F, %:	not less than 5
Fixed Carbon, %:	19-20
Solubility in CS ₂ , %:	greater than 98
Non-mineral matter, insoluble %:	0-1
Mineral matter, %:	trace to 1
Carbenes, %:	0-0.5
Soluble in 88° petroleum naphtha, %:	10-60
Hydrogen, %:	8.5-10
Sulfur, %:	0.3-0.5
Solid paraffines, %:	0-trace
Sulfonation residue, %:	85-95
Saponifiable matter, %:	trace
Minimum Energy Required for Ignition of Dust	26V1
Cloud by Electric Sparks, millijoules:	25
Ignition Temperature of Dust Cloud, °C:	560
Minimum Explosive Concentration of Dust:	20 mg./l. 20
Use in Pyrotechnics: Asphaltum is used as a fuel and binder. It may act as a desensitizer and waterproofing agent.	26Vf 26V1

Additional References :

- 1) "Asphalts and Allied Substances," H. Abraham, D. Van Nostrand Co., Inc., New York (1960)
- 2) "The Science of Petroleum." Vol. 4, A. E. Dunstan et al., eds., Oxford University Press, New York (1938)

AURAMINE HYDROCHLORIDE

Refs.

**(4,4'-Dimethyliminobenzeneimide Hydrochloride,
4,4'-bis (Dimethylamine)Benzhydrylideneimine Hydrochloride,
Imido-tetramethyldiamidodiphylmethane Hydrochloride,
Auramine O, C.I. 41000, C.I. Basic Yellow 2)**

83 (No.425),
82, 48A

Structural Formula : $[(CH_3)_2NC_6H_4]_2C:NH_2Cl$ or $C_{17}H_{22}N_4Cl$ or
 $(H_3C)_2N-C_6H_4-C(=N(CH_3)_2)-C_6H_4-NH_2 \cdot HCl$ or $(H_3C)_2N-C_6H_4-C(=N(CH_3)_2)-C_6H_4-NH_2 \cdot Cl$

Specification No. : **MIL-A-3664 (1962)**

Molecular Weight : **303.84**

Crystalline Form : **flakes**

Color : **yellow**

88V14

Apparent Density, g./ml. : **0.35 ± 0.1**

spec.

Coefficient of Thermal Expansion : _____

Heat of Formation : _____

Free Energy of Formation : _____

Entropy : _____

Meiting Point : **540°K (267°C)**

88V14

538°K (265°C)

Addnl. Ref. 1

Heat of Fusion : _____

Boiling Point : _____

Transition Point : _____

Heat of Sublimation : _____

Heat Content or Enthalpy : _____

Heat Capacity : _____

Decomposition Temperature : _____

Decomposition Products: **The aqueous solution decomposes at about 70°C to NH_4Cl and tetramethyldisminobenzophenone (Michler's Ketone).**

52

The same reaction takes place in cold dilute acid.

Addnl. Ref. 2

Increase in temperature and acidity increases the rate of hydrolysis.

Vapor Pressure : _____

X-Ray Crystallographic Data : _____

Hygroscopicity : _____

Solubility :

In water and alcohol:

slightly soluble

88V14 II

In chloroform :

readily soluble

In ether or pyridine :

almost insoluble

Hydrolyzed by hot water (see Decomposition Products)

Auramine Hydrochloride (page 2)

Wealth Hazard : Carcinogenic an chronic exposure, moderately toxic. ~~The spec.~~ requires that each container be **labeled**. "CAUTION : AVOID SKIN CONTACT. USE WITH ADEQUATE VENTILATION."

92, 93

Safety Classifications :

OSM : not listed

ICC: not listed

Fire and Explosion Hazard:

Electrostatic Sensitivity :

Use in Pyrotechnics: To produce yellow colored smoke.

Additional References :

- 1) J. Chem, Soc. **461** (1940) (also gives absorption spectra)
- 2) J. Am. Chem. Soc. **46, 2343** (1924) ; C.A. **18,3872** (1924)

BARIUM CARBONATE, BaCO₃
(Witherite)

Specification No.:	JAN-B-624	
Molecular Weight:	197.37	
Crystalline Form:	(witherite, γ) rhombic (α) hexagonal	1
Color:	white	1
Density, g./ml.:	(solid) 4.43 (witherite) 4.29	1A 31A
Coefficient of Thermal Expansion, cubical:	2.33×10^{-6} (value used commercially)	31
Heat of Formation, Kcal./mole at 298°K:	(c) -291.3	1, 9
Free Energy of Formation, Kcal./mole, at 298°K:	(c) -272.2	1, 9
Entropy, cal./deg./mole, at 298°K:	(c) 26.8	3, 7, 9
See table below		
Melting Point, at 90 atm.:	2013°K (1740°C) fuses at 1361°C with loss of CO ₂	1 52V1
Heat of Fusion:	—	
Boiling Point:	decomposes at 1723°K (1450°C) with loss of CO ₂	22
Heat of Vaporization:	—	
Transition Point:	α 1079°K (806°C) $\rightarrow$ β β 1241°K (968°C) $\rightarrow$ γ	4
Heat of Transition, cal./mole:	α 4490 $\rightarrow$ β 730 $\rightarrow$ γ	4
Heat of Sublimation:	—	
HEAT CONTENT AND ENTROPY OF BaCO ₃ (c) (Base, α -crystals at 298.15°K)		4

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	2300	6.61	1100	27,060	39.17
500	4730	12.03	1200	30,760	42.39
600	7330	16.76	1241 (β)	32,270	43.62
700	10,080	21.00	1241 (γ)	33,000	44.21
800	12,980	24.87	1300	35,240	45.98
900	16,020	28.45	1400	39,040	48.79
1000	19,190	31.79	1500	42,840	51.41
1079 (α)	21,790	34.29	1600	46,640	53.86
1079 (β)	26,280	38.45			

Barium Carbonate, BaCO₃ (page 2)

BaCO₃ (α):

Enthalpy: $H_T - H_{298.15} = 21.50T + 5.53 \times 10^{-3}T^2 + 3.91 \times 10^{-5}T^3 - 8213$
(0.5 percent; 2980–1079°K)

Heat Capacity: $C_p = 21.50 + 11.06 \times 10^{-3}T - 3.91 \times 10^{-5}T^2$

BaCO₃ (β):

Enthalpy: $H_T - H_{298.15} = 37.00T - 13,644$ (0.1 percent; 1079°–1241°K)

Heat Capacity: $C_p = 37.00$

BaCO₃ (γ):

Enthalpy: $H_T - H_{298.15} = 38.00T - 14,160$ (0.1 percent; 1241–1600°K)

Heat Capacity: $C_p = 38.00$

Decomposition Products:

For pyrolysis **see** Ref. 45 and Addnl. Ref. 1

Decomposition Products:

BaO + CO₂.

Dissociation Pressure:

Press, mm.	0	5	45	120	240	340	450	675	760
Temp. °C	997	1017	1057	1097	1137	1157	1177	1197	1200

54V3

For Dissociation Pressure **see** also Addnl. Ref. 3

Calculated Dissociation Pressures to BaO + CO₂ above 1079°K are given by
 $\log P_{\text{mm.}} = \frac{13,075}{T} + 7.668$

Addnl. Ref. 3

Vapor Pressure of CO₂ at 1100°C:

20 mm.

52V1

At 1600°C the loss of CO₂ is complete

See also Addnl. Ref. 2

X-Ray Crystallographic Data:

System	Space Group	a	b	c	Molecules/Unit Cell
rhombic	V _h ¹⁶	5.29	8.88	6.41	4

1

Hygroscopicity:

Solubility Data: In 100 ml. water:

α = 0.002 g. at 20°C
0.006 g. at 100°C
β = 0.0022 g. at 18°C
0.0065 g. at 100°C

1

In acids, NH₄Cl:

soluble

In alcohol:

insoluble

Health Hazard: Poisonous. Irritates mucous membranes. It produces dermatitis and causes hemorrhages in the gastrointestinal tract and kidneys.

12, 29

M.A.C., mg./m.³:

0.5

Barium Carbonate, BaCO₃ (page 3)

Safety Classifications :

OSM:

not listed

ICC :

not listed

Fire and Explosion Hazard:

none listed

Electrostatic Sensitivity :

—

Use in Pyrotechnics : BaCO₃ is used as a retardant. It imparts some green color to a burning composition. 17

Additional References :

- 1) "Differential Thermal Analysis Studies of Ceramic Materials : Characteristic Heat Effects of Some Carbonates," M. Gruver, J. Am. Ceram. Soc. **33, 96 (1950)**
- 2) G. Tammann and W. Pape, Zeit. anorg. Chem. **127, 50 (1923)**
- 3) "Experimental Heat Contents of SrO, BaO, CaO, BaCO₃ and SrCO₃ at High Temperatures. Dissociation Pressures of BaCO₃ and SrCO₃," J. J. Lander, J. Am. Chem. Soc. **73, 5794 (1951)**

BARIUM CHLORATE, Ba(ClO₃)₂

Refs.

Percent Oxygen :	31.55						
Specification No. :	not listed						
Molecular Weight:	304.27						
Crystalline Form :	—						
Color :	colorless						
Density, g./ml. :	(solid) 3.856 at 24°C	12					
Coefficient of Thermal Expansion :	—						
Heat of Formation, Kcal./mole at 298°K :	(c) -181.7	LA 9					
Free Energy of Formation, Kcal./mole at 298°K :	(c) -133.1	14S30					
Entropy, cal./deg./mole at 298°K :	53.7	44S30					
Melting Point:	414	1A					
Heat of Fusion :	—						
Boiling Point :	—						
Transition Point:	—						
Heat of Sublimation :	—						
Heat Content or Enthalpy:	—						
Heat Capacity of Ba (ClO ₃) ₂ • H ₂ O, cal./deg./mole :							
C _p = 50.6 (289-320°K)		4					
Decomposition Temperature : Decomposition starts at about 300°C.		54V2					
For DTA see Ref. 33							
Decomposition Products:	Ba (ClO ₄) ₂ + 2O ₂	54V2					
Vapor Pressure:	—						
X-Ray Crystdographic Data for Ba (ClO ₃) ₂ • H ₂ O :							
System	Space Group	a	b	c	Axial Angle	Molecules/ Unit Cell	Addn
monoclinic	C _{2h}	8.86	7.80	9.35	β = 94° ± 1/2°	4	
See also Addnl. Ref. 1							
Hygroscopicity :	—						
Solubility Data :							
In water (g./100 g. solvent) :					20.35 at 0°C		31
					84.8 at 80°C		
Health Hazard : Poisonous when taken by mouth. Very toxic in contact with the skin, when inhaled as a dust, or when ingested.							29, 1
M.A.C., mg./m. ³					0.5		12
Safety Classifications							
OSM :	Class 1, in original container or equivalent. Class 2, not in original container or equivalent.						
ICC :	Oxidizing material, yellow label. Listed under Explosives and Other Dangerous Articles.						
M.C.A. :	Warning label required.						

Barium Chlorate, $\text{Ba}(\text{ClO}_3)_2$ (page 2)

Fire and Explosion Hazard: Considered **more dangerous to** store than KClO_3 . **14, 12**
Should be stored **away from** flammable materials because of possible fire and explosion.

Electrostatic Sensitivity : _____

Ignition Temperature, $^{\circ}\text{C}$: (5 second point) 506 **33**

Activation Energy, Kcal./mole : 45.7 **33**

Use in Pyrotechnics:

To impart a green color to burning compositions, and **as** an oxidizing agent.

Additional References :

- 1) "Determination **of** the Structure of Metallic Chlorates by Infrared Spectroscopy," T. Dupuis, **Compt. rend. 242, 2922 (1956). C. A. 50, 15,236 (1956)**
- 2) "Unit Cell and Space Group of Barium Chlorate Monohydrate," G. Kartha, Current Science (India) **20, 151 (1951). C. A. 46,4312 (1952)**

BARIUM CHLORIDE, BaCl ₂							Refs.
Specification No.:	not listed						
Molecular Weight:	208.27						
Crystalline Form:	monoclinic						1A
Color:	colorless						1A
Density, g./ml.:	(solid) 3.856 at 24°C						1A
Density of Molten BaCl ₂							
Temp. °C	964	975	1025	1050	1085	1100	44S30
Density	3.057	3.052	3.015	3.108	3.087	3.076	
For the temp. range 964°-1100°C the density is given by the formula $D = 3.032 - 0.00070 (t - 1000)$							
Note: See refs. for additional density formulas							
Coefficient of Thermal Expansion, cubic, 20-170°C:	60 × 10 ⁻⁶						44330
Heat of Formation, Kcal./mole at 298°K:	(c) -205.66						1A, 6
Free Energy of Formation, Kcal./mole at 298°K:	(c) -193.8						1A, 9
Entropy, cal./deg./mole at 298°K:	30						1A, 9
Melting Point, °K:	1235						9
Heat of Fusion, Kcal./mole at 1235°K:	5.4						9, 24A
Boiling Point, °C:	1560						1A, 31A
Heat of Vaporization, Kcal./mole:	50.0						24A
	57						41
Transition Point, monoclinic (α) to cubic β:	1198°K 920-930°C						1A, 9, 6 44S30
Heat of Sublimation, Kcal./mole:	57						44330
Heat Content or Enthalpy:	—						
Heat Capacity, cal./deg./mole:	(solid) 18.0 at 25°C						
$C_p = 17.00 + 334 \times 10^{-6} T$ (estd., 298-1198°K)							4
Decomposition Temperature: None up to 1000°C (max. experimental temp.)							33
Decomposition Products:	—						
Vapor Pressure (liquid BaCl ₂):							
Press. mm.	about 0.7	4.4	6.2	8.5	760		44S30
Temp. °K	1342.9	1435.2	1465.9	1486.7	1835		
X-Ray Crystallographic Data:							
	System	Space Group	a	b	c	Molecules/ Unit Cell	
BaCl ₂	orthorhombic	V _h ¹⁶	9.333	7.822	4.705	4	18, 96, Addnl.
BaCl ₂ · 2H ₂ O	orthorhombic	D _{2h} ¹⁶	4.51	9.02	11.28		Ref. 1

Barium Chloride, BaCl₂ (page 2)

Hygroscopicity:	slight	44S30
Solubility Data:		
In H ₂ O, g./100 ml.:	31 at 0°C 59 at 100°C	31A
In HCl, HNO ₃ :	slightly soluble	
In alcohol:	insoluble	
Health Hazard:		
Extremely toxic. Fatal dose 0.8 to 0.9 g.		29
Safety Classifications:		
OSM:	not listed	
ICC:	not listed	
Fire and Explosion Hazard:	none listed	
Electrostatic Sensitivity:	—	
Use in Pyrotechnics: BaCl ₂ results from the burning of some barium compounds in the presence of chlorine compounds.		8
Additional References:		
1) C.A. 44, 897 (1950)		

BARIUM CHROMATE, BaCrO ₄ , (Lemon Chrome, Ultramarine Yellow, Baryta Yellow Gelbin)						Refs. 1, 11, 25
Percent Oxygen :	25.26					
Specification No. :	MIL-B-550					
The specification covers two grades; grade A is for use in delay and non-gaseous powder, grade B for use in pyrotechnic mixtures.						
Molecular Weight :	253.37					
Crystalline Form:	rhombic					1
Color :	yellow					1
Density, g./ml. :	4.498					1
Coefficient of Thermal Expansion (calculated from lattice constants), linear :						44S30 sup
Temp. Range °C	10-70	70-130	130-190	190-250	10-250	
Coeff. × 10 ⁵	1.75	1.73	1.57	1.65	1.67	
Heat of Formation, Kcal./mole at 298°K :	(c) -341.3					1, 9
Free Energy of Formation, Kcal./mole at 298°K :	-315.96					78
Entropy, cal./deg./mole at 298°K :	34.7					78
Melting Point :	decomposes (see below)					
Heat of Fusion :	decomposes (see below)					
Boiling Point :	decomposes (see below)					
Transition Point :	—					
Heat of Sublimation :	—					
Heat Content or Enthalpy :	—					
Heat Capacity :	—					
Decomposition Temperature and Products : When heated, starts to lose weight at about 60°C. On further heating very slowly loses weight even up to 1015°C, at which point it is a mixture of the yellow chromate and green chromite. Even at this temperature the loss is less than 1%.						Addnl. Re
Vapor Pressure :	—					
X-Ray Crystallographic Data :	—					
Hygroscopicity : Gain in weight (%) at 70°F of specification grade A material						
Exposure hrs.		Relative Humidity, %				33
		52	75.8	90		
24		0.06	0.05	0.25		
48		0.06	0.06	0.27		
72		0.06	0.06	0.27		
144		0.06	0.09	0.28		
168		0.06	0.09	0.28		
Solubility Data : In water, g./100 g. :						1
In mineral acids:						

Barium Chromate, BaCrO₄ (page 2)

Health Hazard : Poisonous. ~~Has~~ a corrosive action on the skin and mucous membranes. Produces dermatitis. 12, 29

The specification requires that all containers be marked with the following precautionary marking: "AVOID **INHALATION** OF DUST. AVOID **PROLONGED OR REPEATED** CONTACT WITH **SKIN**."

Δ M.A.C. (as **CrO₃**) for an 8-hr. day: 0.1 mg./m.³ 14

Safety Classification :

OSM : class 2

ICC : —

U.N. : poisonous (toxic)

Fire and Explosion ~~Hazard~~ : Emits highly **toxic** fumes **when heated**. An oxidant which reacts vigorously with reducing materials. 12

Electrostatic Sensitivity : —

Use in Pyrotechnics: Barium chromate is used as an oxidizing agent, and to impart a green color to a burning composition. 17

Additional References :

- 1) S. Peltier and C. Duval, Anal. Chim. Acta 1, 361 (1947)

BARIUM NITRATE, Ba(NO₃)₂
(Nitrobarite)

Refs.

Percent Oxygen :	36.73	
Specification No. :	MIL-B-162B	
The specification covers six classes that differ in purity and granulation. The following four classes are used in pyrotechnics:		
Class 1 , used in priming compositions (in two granulations) ;		
2 , used in photoflash compositions;		
5 , used in incendiary mixtures;		
6 , used in pyrotechnic compositions.		
Molecular Weight :	261.38	
Crystalline Form :	cubic	1
Color :	colorless	1
Density, g./ml. :	(solid) 3.24 at 23°C	1
Coefficient of Thermal Expansion, linear, -78° to +15°C :	5×10^{-5}	44S30 sup
Heat of Formation, Kcal./mole at 298°K :	-237.06	1, 9
Free Energy of Formation , Kcal./mole at 298°K :	- 190.0	9
Entropy, cal./deg./mole at 298°K :	51.1	9

HEAT CONTENT AND ENTROPY OF Ba(NO₃)₂(c)
(Base, crystals at 298.15°K; mol. wt., 261.38)

4

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	3960	11.39	700	18,460	38.14
500	8410	21.30	800	24,070	45.62
600	13,240	30.10	850	27,020	49.20

Ba(NO₃)₂(c) :

Enthalpy : $H_T - H_{298.15} = 30.05T + 17.85 \times 10^{-5}T^2 + 4.01 \times 10^{-8}T^3 - 11,891$
(0.2 percent ; 298° - 850°K)
Heat Capacity : $C_p = 30.05 + 35.70 \times 10^{-5}T - 4.01 \times 10^{-8}T^2$

Melting Point :	868°K	7, 9
Heat of Fusion, Kcal./mole:	6	9
Boiling Point :	decomposes	1
Transition Point :	—	
Heat of Sublimation :	—	
Heat Capacity, cal./deg./mole at 298°K :	(solid) 36.1	9
See equation under table above		

Barium Nitrate, Ba(NOS)₂ (page 2)

Decomposition Temperature :	555–600°C	Addnl. Ref. 1
For DTA see Refs. 33 and 47		
For TAG see Ref. 33		
Decomposition Products :	evolves NO ₂ and O ₂	20V3
Vapor Pressure :	—	
X-Ray Crystallographic Data :		
System	Space Group	a
cubic	T _h ^h	8.11
		Molecules/ Unit Cell
		4
Hygroscopicity :		
Gain in mg./g. at equilibrium at R.T. :	purified < 0.1 at 75% and 86% R.H. 0.6 at 93% R.H.	32
Solubility Data :		
In water (g./100 g.) at °C :	8.7 at 20° ; 34.2 at 100°	1
In acids:	slightly soluble	
In alcohol, conc. nitric acid :	insoluble	
Health Hazard : Moderately poisonous. Irritates eyes, ears, nose, throat, and skin ; produces dermatitis. When heated evolves toxic fumes. Produces gastrointestinal irritation.		93, 29, 12, 20, 50V7
M.A.C.	0.5	14
Safety Classifications :		
OSM : Class 1 when packed or shipped in original containers or equivalent.		
ICC :	Oxidizing material ; yellow label	
Fire and Explosion Hazard : By itself the fire hazard is moderate. As a strong oxidizing agent it reacts vigorously when heated with reducing materials and may even result in detonation.		12
Electrostatic Sensitivity :	—	
Use in Pyrotechnics: Barium nitrate is used as an oxidizer, and to impart a green color to burning compositions.		17
Storage: Keep barium nitrate in a moisture-proof container in a dry place to prevent caking.		
Additional References :		
1) C.A. 49,12932 (1955)		

BARIUM' OXALATE, BaC_2O_4		Refs.
Specification No. :	JAN-B-660	
Molecular Weight:	225.38	
Crystalline Form :	—	
Color :	colorless	1
Density, g./ml. :	(solid) 2.658	1
Coedicient of Thermal Expansion :	—	
Heat of Formation, Kcal./mole at		
18°C (c) BaC_2O_4 :	327.6	Addnl. Ref. 1
25°C (c) $\text{BaC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$:	363.7	1
18°C (ppt.) $\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$:	-397.37	1
25°C $\text{BaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$:	-470.1	9
25°C $\text{BaC}_2\text{O}_4 \cdot 3.5\text{H}_2\text{O}$:	-575.73	9
Free Energy of Formation:	—	
Entropy :	—	
Melting Point:	—	
Heat of Fusion:	—	
Boiling Point:	decomposes	
Heat of Vaporization:	—	
Transition Point:	—	
Heat of Sublimation :	—	
Heat Content or Enthalpy:	—	
Heat Capacity :	—	
Decomposition Temperature :	loses CO above 846°C	46
Decomposition Products :	$\text{CO} + \text{BaCO}_3$	
Vapor Pressure :	—	
X-Ray Crystallographic Data :	—	
Hygroscopicity :	—	
Solubility Data: In water, g./ml. solvent:	0.0093 at 18°C	1
	0.0228 at 100°C	
In acids, NH_4Cl :	soluble	
In alcohol:	insoluble.	
Health Hazard: Poisonous. Irritates eyes, nose, throat, and skin. Produces dermatitis.		12, 29
Safety Classifications:		
OSM:	not specifically mentioned	
ICC:	not specifically mentioned	
U.N. :	class 6 (a)—poisonous toxic substance	

Barium Oxalate, BaC_2O_4 (page 2)

Fire and Explosion Hazard : Dangerous when heated to decomposition; emits toxic fumes. 12

Electrostatic Sensitivity : —

Use in Pyrotechnics: As a retardant. Imparts some green color to burning compositions. 17

Additional References :

- 1) L. Médard, *Mém. artillerie franç*, **28**, 467 (1954)

BARIUM OXIDE, BaO

(Barium Meroxide, Baryta, Barium Protoxide, Calcined Baryta)

Specification No.:	—	Refs.
Molecular Weight:	153.36	1, 11, 12, 29
Crystalline Form:	cubic or hexagonal	1
Color:	colorless	1
Density, g./ml.:	(solid) 5.72 (hex) 5.32	1
Coefficient of Thermal Expansion:	3.0×10^{-4}	47
Heat of Formation, Kcal./mole at 298°K:	(c) -133.4	1, 9
Free Energy of Formation, Kcal./mole at 298°K:	(c) -126.3	1, 9

a. HEAT AND FREE ENERGY OF FORMATION OF BaO(c)

(Mol. wt., 153.36)

T, °K	A H (cal./mole)	A F° (cal./mole)
298.16 . . .	-133,500(± 3000)	-126,500(± 3500)
400	-133,000	-124,000
533	-133,000	-121,500
600	-133,000	-119,500
648	-132,500	-118,500
648	-133,000	-118,500
700	-132,500	-117,000
800	-132,500	-115,000
900	-132,500	-113,000
977	-132,000	-111,000
977	-134,500	-111,000
1000	-134,500	-110,500
1100	-184,000	-108,000
1200	-134,000	-106,000
1300	-133,500	-103,500
1400	-133,500	-101,500
1500	-133,000	-99,000
1600	-133,000	-96,500
1700	-132,500	-94,500
1800	-132,500	-92,000
1900	-132,000	-90,000
1911	-132,000	-90,000
1911	-167,500	-90,000
2000	-167,000	-86,000

Rarium Oxide, BaO (page 2)

Phase Changes of Metal

T.P. ($\alpha \rightarrow \beta$), 648°K

$\Delta H = 140 \text{ cal./g.-atom}$

M. Y. 977°K; $\Delta H = 2250 \text{ cal./g.-atom}$

B. P., 1911°K; $\Delta H = 35,660 \text{ cal./g.-atom}$

Free Energy Equations:

Reaction	Range of Validity, °K	
1) Ba (α) + $\frac{1}{2}$ O ₂ (g) = BaO (c)	298.16 to 648	2
$\Delta F_T^\circ = -134,590 - 7.60T \log T + .87 (10^{-3}T^2) + .42 (10^6T^{-1}) + 45.76T$		
2) Ba (β) + $\frac{1}{2}$ O ₂ (g) = BaO (c)	648 to 977	
$\Delta F_T^\circ = -134,140 - 3.34T \log T - .56 (10^{-3}T^2) + .42 (10^6T^{-1}) + 34.01T$		
3) Ba (l) + $\frac{1}{2}$ O ₂ (g) = BaO (c)	977 to 1911	
$\Delta F_T^\circ = -135,900 - 2.19T \log T - .56 (10^{-3}T^2) + .42 (10^6T^{-1}) + 32.37T$		
4) Ba (g) + $\frac{1}{2}$ O ₂ (g) = BaO (c)	1911 to 2000	
$\Delta F_T^\circ = -176,400 - 8.01T \log T - .56 (10^{-3}T^2) + .42 (10^6T^{-1}) + 72.66T$		

Entropy, cal./deg./mole at 298°K: (solid) 16.8 ± .03
(gas) 55.9 ± .5 1, 3, 9

See Tables b and c

Melting Point: 2190°K (1917°C) 9

Heat of Fusion, Kcal./mole: 13.8 ± 2.0 24

Boiling Point: about 2273°K (2000°C) 1

Transition Point: ———

Heat of Sublimation, cal./mole: 90.0 24

b. HEAT CONTENT AND ENTROPY OF BaO (c) (Base, crystals at 298.15°K; mol. wt., 153.36) 4

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	1170	3.36	1300	13,090	18.77
500	2380	6.07	1400	14,520	19.83
600	3660	8.40	1500	15,970	20.83
700	4980	10.43	1600	17,440	21.78
800	6300	12.20	1700	18,920	22.67
900	7620	13.75	1800	20,420	23.53
1000	8950	15.15	1900	21,930	24.35
1100	10,300	16.44	2000	23,450	25.13
1200	11,680	17.64			

Barium Oxide, BaO (page 3)

BaO (c) :

Enthalpy : $H_T - H_{298.15} = 11.79T + 0.94 \times 10^{-5}T^2 + 0.88 \times 10^{-8}T^3 - 3894$
(0.5 percent; 298° - 2000°K)

Heat Capacity : $C_p = 11.79 + 1.88 \times 10^{-5}T - 0.88 \times 10^{-8}T^2$

4

c. HEAT CONTENT AND ENTROPY OF BaO (g)
(Base, ideal gas at 298.15°K; mol. wt., 153.36)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	820	2.36	1000	5985	10.21
500	1650	4.21	1200	7750	11.82
600	2500	5.76	1400	9520	13.18
700	3365	7.10	1600	11,295	14.37
800	4235	8.26	1800	13,075	15.42
900	5910	9.29	2000	14,855	16.35

BaO (g) :

Enthalpy : $H_T - H_{298.15} = 8.621 + 0.10 \times 10^{-5}T^2 + 0.67 \times 10^{-8}T^3 - 2804$
(0.3 percent; 298° - 2000°K)

Heat Capacity : $C_p = 8.62 + 0.20 \times 10^{-5}T - 0.67 \times 10^{-8}T^2$

4

Decomposition Temperature : } When heated in air at 450°C, it combines
Decomposition Products : } with O and forms BaO₂. On further heating
above 600°C, BaO₂ loses O and reforms BaO.

Vapor Pressure : 0.00076 mm. at 1650°K
For the range 900-1200°C : $\log P = -(19400/T + 8.69)$

29

41
Addnl. Ref. 1

X-Ray Crystallographic Data :

System	Space Group	a	Molecules/Unit Cell
cubic	O _h	5.50	4

1

Hygroscopicity: Absorbs water with formation of Ba(OH)₂ with evolution of much heat.

29

Absorbs moisture and CO₂ on exposure to air and forms BaCO₃.

Caution : Keep in tightly closed container,

Solubility Data: In water:

1.5 g./ml., decomposes
90.8 g./100 ml. at 80°C

1

In dil. acids, alcohol :

soluble

29

In CH₃OH, C₂H₅OH :

slowly soluble

In NH₃, acetic acid:

insoluble

Health Hazard : Poisonous. Irritates eyes, ears, nose, throat, and skin. Produces dermatitis. Gastrointestinal irritant:

12, 29, 50V7

M.A.C. :

0,5

14

Barium Oxide, **BaO** (page 4)

Safety Classifications:

OSM :	not specifically listed
ICC :	not specifically listed
U.N.:	classified under "Poisonous (toxic) substances."

Fire and Explosion Hazard : Produces considerable heat on contact with water or ~~steam~~. ~~Some~~ hazard by chemical reaction.

12

Electrostatic Sensitivity : _____

Use in Pyrotechnics: BaO is a product of the burning of many barium compounds.

Additional References:

- 1) C.A. **52**, 3446 (1958)

BARIUM PERCHLORATE, Ba(ClO ₄) ₂					Refs.
Percent Oxygen :	38.06				
Specification No. :	—				
Molecular Weight :	336.27				
Crystalline Form :	hexagonal				
Color :	colorless				
Density, g./ml. :	(solid) (3H ₂ O) 2.74				29
Coefficient of Thermal Expansion :	—				
Heat of Formation, Kcal./mole at 298°K :	(c) -192.8				1, 9
Free Energy of Formation:	—				
Entropy, cal./deg./mole at 298.16°K :	57.7				36
Melting Point:	687°K (414°C)				1
	778°K (505°C)				35
Heat of Fusion :	—				
Boiling Point:	decomposes at 673°K (400°C)				12
	decomposes above 793°K (520°C)				Addnl. Ref. 1
Heat of Vaporization :	—				
Transition Points :	α to β at 557°K (284°C)				72
	β to γ at 633°K (360°C)				
Heat of Sublimation :	—				
Heat Content or Enthalpy:	—				
Heat Capacity :	—				
Decomposition Temperature :	vigorous decomposition at 504°C				47
Decomposition Products :	BaCl ₂ and O ₂				Addnl. Ref. 1
For DTA and TGA see Ref. 33					
Vapor Pressure :	—				
X-Ray Crystallographic Data :					
System	Space Group	a	b	c	Molecules/Unit Cell
rhombic	V _h ¹⁶	5.29	8.88	6.41	4
Hygroscopicity :	—				
Solubility Data : In water, g./100 ml. :	198.5 at 25°; very sol. hot				65
Solubility in Nonaqueous Solvents, at 25°C:					65, 77
Solvent	g./100 g. solvent				
acetone	124.7				
n-butyl alcohol	58.18				
ethyl acetate	112.9				
furfural (at 20°C)	43				
methyl alcohol	217.1				
n-propyl alcohol	75.65				

Barium Perchlorate, $\text{Ba}(\text{ClO}_4)_2$ (page 2)

Health Hazard: $\text{Ba}(\text{ClO}_4)_2$ is poisonous, irritates the eyes, nose, throat, and produces dermatitis. It may affect the central nervous system and kidneys. Its harmful effects are mainly due to the barium ion. Gastrointestinal irritant.

Caution: Avoid skin contact.

MAC. :

0.5

12, 26, 29,
50V7

65
14

Safety Classifications:

OSM: Class 1. ~~Class 2~~ when not packed in original shipping container or equivalent.

ICC: Oxidizing material, yellow label. Listed under "Explosives and Other Dangerous Articles."

Fire and Explosion Hazard: $\text{Ba}(\text{ClO}_4)_2$ is dangerous because it may be exploded by shock, heat, or chemical reaction. It forms explosive mixtures with carbonaceous material, S, powdered Mg, and Al. It emits highly toxic fumes when heated. Fires involving perchlorates alone may be fought with water.

12, 14

Electrostatic Sensitivity: —

Used in Pyrotechnics: $\text{Ba}(\text{ClO}_4)_2$ is used as an oxidizer, and to give a green color to burning compositions.

17

Additional References:

- 1) C.A. 51, 2439 (1957)

BARIUM PEROXIDE, BaO₂

(Barium Dioxide, Barium Superoxide, Barium Binoxide)

Refs.

1, 29

Percent Oxygen :	18.89	
Specification No. :	JAN-B-153 (1)	
The specification covers one grade and three classes that differ in granulation.		
Molecular Weight :	169.36	
Crystalline Form :	powder	1
Color:	white to grey	1
Density, g./ml. :	(solid) 4.96	1
Coefficient of Thermal Expansion :	—	
Heat of Formation, Kcal./mole at 298°K:	-150.5	1, 9
Free Energy of Formation:		

HEAT AND FREE ENERGY OF FORMATION OF BaO₂ (c)

(Mol. wt., 169.36)

2

T, °K	Δ H (cal./mole)	Δ F° (cal. /mole)
298.16 . .	-153,000 (± 6000)	-140,500 (± 6000)
400	-153,000	-136,500
500	-152,500	-132,000
600	-152,000	-128,000
648	-152,000	-126,500
648	-152,000	-126,500
700	-152,000	-124,000
800	-151,500	-120,500
900	-151,000	-116,500
977	-151,000	-118,500
977	-153,000	-113,500
1000	-153,000	-112,500
1100	-152,500	-108,500
1200	-152,500	-104,500
1300	-152,000	-100,500
1400	-151,500	-96,500
1500	-151,000	-92,500

Phase Changes of Metal

T.P. (α→β), 648°K;

Δ H = 140 cal./g.-atom

M.P., 977°K; Δ H = 2250 cal./g.-atom

Barium Peroxide, BaO₂ (page 2)

Free. Energy Equations:

<i>Reaction</i>	<i>Range of Validity, °K</i>	
1) Ba(α) + O ₂ (g) = BaO ₂ (c) ΔF _T ^o = -154,830 - 11.05T log T + .87 (10 ⁻³ T ²) + .42 (10 ⁵ T ⁻¹) + 74.48T	298.16 to 648	2
2) Ba(β) + O ₂ (g) = BaO ₂ (c) ΔF _T ^o = -154,380 - 679T log T - .56 (10 ⁻³ T ²) + .42 (10 ⁵ T ⁻¹) + 62.73T	648 to 977	
3) Ba(l) + O ₂ (g) = BaO ₂ (c) ΔF _T ^o = -156,140 - 5.64T log T - .56 (10 ⁻³ T ²) + .42 (10 ⁵ T ⁻¹) + 61.092T	977 to 1500	
Entropy, cal./deg./mole at 298°K :	(c) 18.6	6
Melting Point:	723°K (450°C)	1
Heat of Fusion, Kcal./mole :	5.7	6
Boiling Point :	loses O at 1073°K (800°C) decomposes at 1110°K (837°C) at 1 atm.	1 8
Transition Point :	—	
Heat of Sublimation :	—	
Heat Content or Enthalpy :	—	
Heat Capacity:	—	
See Ref. 2		
Decomposition Temperature, °C :	800	1
For DTA see Ref. 33		
Decomposition Products :	BaO + O	29 and Addnl. Refs. 1, 2, 3

Vapor Pressure :

Dissociation Press. : 760 mm. at 795°C Addnl. Ref. 1

Press. atm.	0.0149	0.0861	0.1855	0.945	1.220	1.534	42V7
Temp. °K	891.1	970.1	1010.1	1108.1	1126.1	1141.1	

X-Ray Crystallographic Data :

<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>c</i>	<i>Molecules/Unit Cell</i>	
tetragonal	O _h ^{4h}	5.34	6.77		1
	D _{4h} ^{4h}	5.39	6.85	4	97V6

Hygroscopicity : Slowly decomposes in air and on contact with water. Combines with water to form BaO₂·8H₂O

Gain in mg./g. at R.T. after equil. was established in vac. desic.

Reagent Grade :

R.H.%	65	75	86	93	32
24 hrs.	0.6	6.0	28.7	48.0	
Equil.	10	8.6	73.1	126.0	

Solubility Data: In cold water: very soluble
In hot water: decomposes
In dilute acids: soluble; with decomposition forming H₂O₂
In acetone: insoluble

Barium Peroxide, BaO₂ (page 3)

Health Hazard: BaO₂ is poisonous. It irritates the eyes, nose, and throat, and produces dermatitis. Gastrointestinal irritant. 29, 12, 50V7

M.A.C.: 0.5 14

Safety Classifications:

OSM: ~~Class~~ 1. Class 2 when not packed in original containers or equivalent.

ICC: Oxidizing material; yellow label.

Fire and Explosion Hazard: As an oxidizer it is dangerous when heated with reducing material; may result in detonation. 12

Electrostatic Sensitivity: —

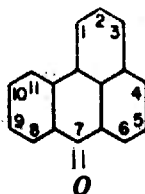
Use in Pyrotechnics: BaO₂ is used as an oxidizer and to impart a green color to burning compositions. It is used in igniter and tracer compositions. 17

Additional References:

- 1) "The Decomposition of Barium Peroxide and the Reactivity of the Resulting Barium Oxide," J. A. Hedvall, *Zeit. anorg. Chem.* **104**, 163 (1918); *J. Chem. Soc. Abstracts* **1919 ii**, 26
- 2) "Kinetics of the dissociation of Ba and Ca peroxides," M. M. Pavlyuchenko and Yu S. Rubinchik, *C.A.* **52**, 19362 (1958)
- 3) "Heating curves for the hydrates of the peroxides of the Group II metals," I. I. Vol'nov, *C.A.* **52**, 19384 (1958)

BENZANTHRONE, C₁₇H₁₀O

(7-oxo-7-benz(d,e)anthraquinone, 7-H-benz(d,e)anthracene-7-one, 7-meso-benzanthrone, Benzan B, Research Vat Golden Yellow GK)



Structural Formula :

Specification No. :

The specification requires :

MIL-B-50074

purity — minimum 77%
water — maximum 1%

Molecular Weight :

230.25

Crystalline Form :

From alcohol or benzene :

orthorhombic

From nitrobenzene :

needles

Color :

pale yellow

Density, g./ml. :

(solid) 1.371

Coefficient of Thermal Expansion :

—

Heat of Formation :

—

Free Energy :

—

Entropy :

—

Melting Point :

447°K (174°C)
446.1°K (173.1°C)

Heat of Fusion :

—

Boiling Point :

—

Transition Point :

—

Heat of Sublimation :

—

Heat Content or Enthalpy :

—

Heat Capacity :

—

Decomposition Temperature, °C :

about 426° (see below)

For DTA and TGA see Refs. 80 and 81

Decomposition Products :

—

Vapor Pressure :

Press. mm.	1	10	40	100	200
Temp. °C	225.0	297.2	350.0	390	426.5 with decompn

Refs.

1
Addnl. Ref. 3

Addnl. Ref. 3

1
Addnl. Ref. 1

1

1

Benzanthrone (page 2)**X-Ray Crystallographic Data:**

<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>Molecules/ Unit Cell</i>
orthorhombic	D ₂	14.57	15.00	5.07	4

For bond lengths see Addnl, Ref. 2

18V III,
Addnl. Ref. 3**Hygroscopicity:**

Solubility Data: at 20°C per 100 g. solvent,

glacial acetic acid:

0.52

benzene:

0.61

chlorobenzene:

2.05

In tetrachlorethane:

soluble

In con. H₂SO₄:

soluble, giving an orange-red color with an olive-green fluorescence

29

89V14

88V7 II

In toluene:

soluble

Health Hazard: **Some, as** indicated by the spec. requirement that "each container shall be conspicuously labeled: '**CAUTION—AVOID SKIN CONTACT; USE WITH ADEQUATE VENTILATION.**'"

Fire and Explosion Hazard:

slight when heated;
emits smoke

12 •

Safety Classifications:

OSM:

not listed

ICC:

not listed

Electrostatic Sensitivity:

Use in Pyrotechnics: To produce a yellow color in smoke grenades.

Additional References:

- 1) "Freezing Point and Purity Data for Some Organic Compounds," C. R. Witschonke, *Anal. Chem.* **26**, 563 (1954)
- 2) "Calculated Bond Lengths in Some Cyclic Compounds. Part II. Benzanthrone, Acedianthrone, and Flavanthrone," T. H. Goodwin, *J. Chem. Soc.* **1955**, 1689
- 3) "Cell Dimensions and Space Groups of Some Carbocyclic Compounds," H. C. Bayd et al., *Acta Cryst.* **7**, 142 (1954)

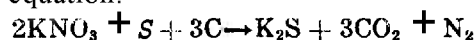
BLACK POWDER

(Gunpowder)

Black powder is an intimate mechanical mixture of potassium or sodium nitrate, charcoal, and sulfur. Willow or alder charcoal and flour of sulfur and 2-3% of water are well mixed in a tumbling barrel. This mixture is transferred to a wheel mill and the desired amount of crystalline potassium nitrate and several percent of water are added. The mill is run for several hours to obtain a uniform mixture. During mixing the mixture is kept damp by the addition of water. The mixture is pressed at about 6000 psi and then broken up by passing between rolls. Broken pieces are screened into sizes and material of undesired size is reconsolidated and passed through rolls and screened. Material of acceptable size is then thoroughly dried in hot air ovens at about 60°C. The material may be polished before drying by rotating it in a tumbling barrel. After tumbling, the black powder is sieved and the fines removed.

Black powder is sensitive to friction, heat, and impact, and is very dangerous to handle. It absorbs moisture and deteriorates rapidly. If kept dry, it will retain its properties indefinitely. Combustible materials that have absorbed liquors leached from black powder are a severe fire hazard and may become explosive. Every safety precaution should be taken in black powder manufacture and operations.

Black powder has a composition close to the stoichiometric proportions needed to satisfy the equation:



In practice, the proportions may be varied slightly.

Formula (specification) :

KNO₃, 74.0%
S, 10.4%
charcoal, 15.6%

specification No. :

JAN-P-223A

(all seven grades listed in the specification are used in pyrotechnics)

Crystalline Form :

mechanical mixture

Color :

black

Density, g./ml. :

approx. 1.6, variable depending mainly on conditions of preparation

Decomposition Temperature : Exothermal preignition reaction starts at about 250°C and culminates at approximately 300°C (DTA and TGA curves).

Decomposition Products :

Hygroscopicity : Black powder is appreciably hygroscopic and is prepared and kept under conditions of low humidity so that its properties will not be adversely affected.

Temp. °C	R.H. %	Gain %
26	75	0.75
25	90	1.91
30	90	2.51

Refs.

13, 50V6

14, 13

13

Addnl. Ref. 4

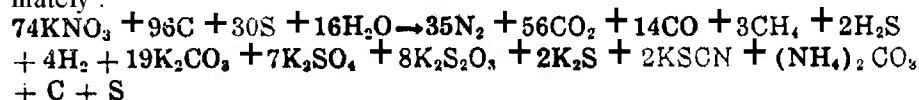
13

Black Powder (page 2)

Explosion Data:

Specific Volume at S.T.P., l./kg.: 285 (H₂O gas)
Explosion Temperature, °C: 2770
Heat of Explosion, Kcal./kg.: 685 (H₂O liquid)
Characteristic Product (V₀Q): 195,200

The equation for the burning of black powder has been given as approximately:



For other equations see Ref. 54V2

Health Hazard: none mentioned

Safety Classifications:

OSM: Class 9 (in charges or containers)

ICC: Class A explosive, not accepted for railway express. Black powder igniters with empty cartridge bags, classified class C explosives.

Fire and Explosion Hazard: Black powder can be detonated by friction, heat, and impact.

Electrostatic*Sensitivity: unconfined > 12.5 joules
energy required to ignition: confined 0.8 joules

Impact Sensitivity, 2 kg. weight falling on 16mg. sample:

Bureau of Mines Apparatus, cm.32 (10% Point)

P.A. Apparatus, in. 16 (10% Point)

Initiating Efficiency (min.wt. in grams required to initiate B.P.):

Igniter Composition K-31: 2.0

Igniter Composition K-29: 2.3

Friction Pendulum Test:

Steel shoe: snaps

Fibre shoe: unaffected

Explosion Temperature Test: (0.02 g. sample in No. 6 copper detonating cap)

Seconds	Temp. °C
0.1 (no cap used)	510
1	490
5	427 ignited
10	356

.75% International Heat Test:

Loss in 48 hrs., weight %: 0.31

Vacuum Stability Tests, cc./hrs. on 5 g. sample: 100°C, 0.5
120°C, 0.9

Sand Test, with 200 g. bomb and 0.4 g. sample of black powder:

Grams sand crushed to pass 30-mesh screen: 8

Sensitivity: tetryl, 0.25 g.

Ballistic Mortar, % of TNT: 50

Addnl. Ref. 5

50V6

14

Addnl. Ref. 6

Following
data on this
page from 13

Black Powder ('page 3)

Trauzl Test, % of TNT:	10
Detonation Rate, meters/sec. at density 1.6:	400
Heat of Explosion, cal./g.:	684
Gas Volume on Explosion, cc./g.	271
Method of Loading:	1) loose (granulated) 2) pressed

Loading Density, g./cc. in thousands of psi:

psi	25	50	60	65	70	75
Density	1.74	1.84	1.86	1.87	1.88	1.89

Method of Storage:	dry
100° Vacuum Stability Test, cc. gas/40 hrs. from a 5 g. sample:	
Initial value:	0.5
After 2 years at 65°C:	0.86
After 2 years at 65°C and 75% R.H.:	1.46

Compatibility with metals:

Dry-compatible with all metals when moisture content is less than 0.2%.
Wet—attacks all common metals except stainless steel.

Destruction:

Black powder may be completely destroyed by leaching or washing with large quantities of water and disposing of the washings separately from the residue.

Use in Pyrotechnics: Black powder is used as an igniter powder, and in time rings (fuzes), fireworks, rockets, Roman candles, and firecrackers.

Additional References:

- 1) "Initiation, Burning and Thermal Decomposition of Gunpowder," J. Blackwood and F. Bowden, Proc. Roy. Soc. 213, 285 (1952)
- 2) "Chemistry of Powder and Explosives," T. L. Davis, John Wiley & Sons, Inc., New York (1943)
- 3) Refs 52V4 and 54V2
- 4) "A Thermoanalytical Study of the Ignition and Combustion of Black Powder," C. Campbell and G. Weingarten, Trans. Faraday Soc. 55, 2221 (1959)
- 5) "Explosives," H. Brunswig, John Wiley & Sons, Inc., New York (1912)
- 6) "Sensitivity of Explosives to Initiation by Electrostatic Discharges," F. W. Brown et al., U.S. Dept. of Interior, Bureau of Mines, R.I. 3852 (1946)

BORON, B

Refs.

Specification No. :	PAPD-451	
Molecular Weight :	10.82	
Crystalline Form :	monoclinic crystals or amorphous powder	1
Color :	yellow or brown	1
Density, g./ml. :	(c) 2.34 (amor.) 2.37 2.35	1A 31A
Coefficient of Thermal Expansion, linear, 20-750°C :	17.4×10^{-6} per °C	27
Heat of Formation, Kcal./mole at 298°K :	(gas) 97.2	1, 9
Free Energy of Formation, Kcal./mole at 298°K :	(gas) 86.7	1, 9
Entropy, Kcal./mole at 298°K :	(c) 1.40 (gas-monatomic) 36.65	5 5
See Table a		
Melting Point :	2313°K (2037 ± 37°C)	31A
Heat of Fusion, cal./mole :	5300	5
Boiling Point :	4198°K (39275°C)	31A
Heat of Vaporization, cal./mole :	128,000	5
Transition Point :	—	
Heat of Sublimation, cal./mole at 298°K :	141,000	5
Heat Content or Enthalpy, cal./mole at 298°K :	292	5
See Tables a and b		
Heat Capacity, cal./deg./mole at 298°K :	(solid) 2.63 (liquid) 7.5 (gas) 4.97	5.9

See equations under Tables a and b

a HEAT CONTENT AND ENTROPY OF B(c, l) (Base crystals at 298.15°K ; atomic wt. 10.82)

4

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	310	0.89	1700	7765	8.61
500	690	1.75	1800	8460	9.00
600	1120	2.52	1900	9165	9.38
700	1600	3.26	2000	9880	9.75
800	2120	3.95	2100	10,605	10.10
900	2670	4.60	2200	11,340	10.45
1000	3245	5.20	2300 (c)	12,080	10.78
1100	3845	5.78	2300 (l)	17,380	13.08
1200	4465	6.31	2400	18,130	13.40
1300	5100	6.82	2600	19,630	14.00
1400	5750	7.30	2800	21,130	14.55
1500	6410	7.76	3000	22,630	15.07
1600	7080	8.19			

Boron, B (page 2)

B(c) :

Enthalpy: $H_T - H_{298.15} = 4.13T + 0.83 \times 10^{-3}T^2 + 1.76 \times 10^{-5}T^3 - 1895$
(2.1 percent ; 298° - 2300°K)

Heat Capacity: $C_p = 4.13 + 1.66 \times 10^{-3}T - 1.76 \times 10^{-5}T^2$

B(l) :

Enthalpy: $H_T - H_{298.15} = 7.50T + 130$ (0.1 percent; 2300° - 3000°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	350	1.00	900	3160	5.40
500	785	1.97	1000	3840	6.12
600	1295	2.90	1100	4535	6.78
700	1870	3.78	1200	5255	7.40
800	2500	4.62			

B(amor.) :

Enthalpy: $H_T - H_{298.15} = 3.34T + 1.98 \times 10^{-3}T^2 + 1.48 \times 10^{-5}T^3 - 1668$
(1.1 percent ; 298° - 1200°K)

Heat Capacity: $C_p = 3.34 + 3.96 \times 10^{-3}T - 1.48 \times 10^{-5}T^2$

c. HEAT CAPACITY OF B

(Solid to 2300°K ; liquid from 2300° to 3000°K)

T, °K	C_p (cal./deg./mole)
298	2.63
400	3.46
800	5.35
1200	6.27
1600	6.78
2000	7.20
2200	7.40
2300 3000	7.50

Decomposition Temperature : _____

Decomposition Products : _____

Vapor Pressure :

Press. mm.	10 ⁻⁸	10 ⁻⁶	10 ⁻⁴	10 ⁻²	1	10 ²	760	M.P.
Temp. °K	1650	1850	2100	2430	2930	3730	4200	2300

56

Boron, B (page 3)

&Ray Crystallographic Data :

System	Space Group	a	c	Molecules/ Unit Cell	
tetragonal	D_{2d}^8 or C_{4v}	8.73A	6.03	50	18
hexagonal		11.98	9.54	180	

See also Ref, 44S13 sup

Hygroscopicity :

Solubility Data: In water:	insoluble (slightly soluble when freshly prepared)	1, 29
In HNO_3 , H_2SO_4 :	soluble	
In alc., eth., alk.:	insoluble	

Health Hazard: Boron is not highly toxic but it is a cumulative poison which affects the central nervous system. 12, 25

Safety Classification:

OSM : Class 2 when not packed in original containers or equivalent.

Fire and Explosion Hazard : Boron dust is dangerous as it can ignite on contact with air and explode. It reacts with oxidizing agents and is a dangerous fire and explosion hazard. It burns with intense heat. In the presence of moisture hydrogen may be evolved. Therefore B should be stored in a dry atmosphere and in a properly vented building. Use only nonsparking tools around B. To fight a fire use no water; use powdered graphite, dolomite salt, or other inert material. At about 600° it ignites and burns with a brilliant green flame. 12, 14, 16

Electrostatic Sensitivity:

Use in Pyrotechnics: Boron is used as a component of non-gaseous fuze powders.

Additional References :

- 1) "Boron," J. A. Kohn et al., eds., Plenum Press, Inc., New York (1960) Proceedings of the Conference on Boron, sponsored by the Institute for Exploratory Research, The U.S. Army Signal Research and Development Laboratory, Fort Monmouth, N.J.

CALCIUM, Ca

Refs

Specification No.:	12056A (tech.)	
Molecular Weight:	40.08	
Crystalline Form:	cubic	1
Color:	silvery white when first cut; tarnishes to blue-grey on exposure to air	29
Density, g./ml.:	(solid) 1.55	1
Coefficient of Thermal Expansion, linear, 0-300°:	22×10^{-4}	36
	cubic, 0-21°:	717×10^{-4}
Heat of Formation, Kcal./mole at 298°K:	(gas) 42.200	5
Free Energy of Formation, Kcal./mole at 298°K:	(gas) 34.138	5
Entropy, cal./deg./mole, at 298°K:	(c) $9.95 \pm .10$	3, 5
	(gas) 36.99	5
See Tables a, b, and c		
Melting Point:	1123°K (850°C)	4, 5
Heat of Fusion, cal./mole:	2070 ± 80	4, 5
Boiling Point:	1765°K (1492°C)	5
Heat of Vaporization, cal./mole:	35,840	5
Transition Point:	α to β 713°K (440°C)	4.5
Heat of Transition, cal./mole:	270	4
Heat of Sublimation, cal./mole, at 298°K:	42,200	5
Heat Content or Enthalpy, cal./mole at 298°K:	(did) 1380	5
See Tables a, b, and c		
Heat Capacity, cal./deg./mole at 298°K:	(solid) 6.30	4, 5
	(liquid) 7.40	
	(gas) 4.97	

a. HEAT CONTENT AND ENTROPY OF Ca(c, l) (Base, α -crystals at 298.15°K; atomic wt., 40.08)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	660	1.90	1123 (β) . . .	6825	10.39
500	1340	3.42	1123 (l) . . .	8895	12.23
600	2055	4.72	1200	9465	12.72
700	2800	5.87	1300	10,205	13.31
713 (α) . . .	2900	6.01	1400	10,945	13.86
713 (β) . . .	3170	6.39	1500	11,685	14.37
800	3850	7.29	1600	12,425	14.85
900	4690	8.28	1700	13,165	15.30
1000	5605	9.24	1800	13,905	15.72
1100	6590	10.18			

Calcium, Ca (page 2)

Ca(α):

Enthalpy: $H_T - H_{298.15} = 5.25T + 1.72 \times 10^{-3}T^2 - 1718$ (0.3percent; 298° - 713°K)

Heat Capacity: $C_p = 5.25 + 3.44 \times 10^{-3}T$

Ca(β):

Enthalpy: $H_T - H_{298.15} = 2.68T + 3.40 \times 10^{-3}T^2 - 472$ (0.1percent; 713° - 1123°K)

Heat Capacity: $C_p = 2.68 + 6.80 \times 10^{-3}T$

Ca(l):

Enthalpy: $H_T - H_{298.15} = 7.40T + 585$ (0.1percent; 1123° - 1800°K)

b. HEAT CONTENT AND ENTROPY OF Ca(g)

(Base, ideal gas at 298.15°K; atomic wt., 40.08)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	505	1.46	1900	7965	9.21
500	1005	2.57	2000	8465	9.46
600	1500	3.48	2200	9470	9.94
700	1995	4.24	2400	10,490	10.39
800	2495	4.90	2600	11,535	10.80
900	2990	5.49	2800	12,615	11.20
1000	3490	6.01	3000	13,745	11.59
1100	3985	6.49	3500	16,880	12.56
1200	4480	6.92	4000	20,670	13.57
1300	4980	7.32	4500	25,250	14.64
1400	5475	7.69	5000	30,685	15.79
1500	5975	8.03	6000	43,870	18.18
1600	6470	8.35	7000	59,365	20.57
1700	6970	8.65	8000	76,140	22.81
1800	7465	8.91			

Ca(g):

Enthalpy: $H_T - H_{298.15} = 4.97T - 1482$ (0.1percent; 298° - 2500°K)

Calcium, Ca (page 3)

c. HEAT CAPACITY OF Ca

Solid I from 298° – 713°K Solid II from 713° – 1123°K		Liquid from 1123° – 1765°K Gas (mon) from 1765° – 3000°K	
T, °K	C _p (cal./deg./mole)	T, °K	C _p (cal./deg./mole)
298	6.30	1200 to	
400	6.64	1700	7.40
600	7.31	1800	4.99
700	7.64	2200	5.06
800	8.08	2600	5.30
900	8.78	3000	5.80
1000	9.49		
1100	10.18		

Decomposition Temperature: —

Decomposition Products: DTA

Vapor Pressure:

Press. " Hg	10	40	100	400	760	M.P.
Temp. °C	983	1111	1207	1388	1487	851

X-Ray Crystallographic Data:

System	Space Group	a	Atoms/Unit Cell
cubic	O _h	5.56	4

Hygroscopicity: Reacts with water (much slower than does sodium) to form Ca(OH)₂ and hydrogen.

Solubility Data: In water:

reacts to form Ca(OH)₂ and hydrogen

In acids:

soluble

In alcohol:

slightly soluble, with which it reacts slowly

In benzene, liquid NH₃, kerosene:

insoluble

Health Hazard:

caustic to all tissues

Safety Classifications:

OSM:

not listed

ICC:

not listed

U.N.:

not listed

Fire and Explosion Hazard. The powdered Metal exposed to air is a dangerous fire hazard. It burns with intense heat and a crimson flame. When compounded with oxidizing agents the powdered metal is both a dangerous fire and explosion hazard. It is a strong reducing agent. Contact with alkali hydroxides or carbonates may cause detonation. Precautions should be taken to prevent water from contacting the material. Store and process it only in rooms or buildings adequately vented at the highest point to prevent

Calcium, Ca (page 4)

accumulation of evolved hydrogen gas which results from the reaction of powdered metal and moisture. In the repair or maintenance of buildings or equipment, powder or dust should be removed and non-sparking tools used. CCl₄ should not be used near calcium as an explosion may occur.

Electrostatic Sensitivity : _____

Use in Pyrotechnics: As a fuel and to impart a crimson color to burning compositions.

Additional References:

- 1) Ref. 94
- 2) C.A. 37,2578 (1942)

Addnl. Ref. 2

CALCIUM CARBONATE, CaCO_3

(Marble, Precipitated Chalk, Whiting, White Chalk, Prepared Chalk, Calcite, Drop Chalk, Paris White, **English White, Iceland Spar)**

Specification No. :	JAN-C-293	<i>Refs.</i>
Molecular Weight :	100.09	1, 11, 29
Crystalline Form :	(aragonite) rhombic (calcite) hexagonal	1
Color :	colorless	1
Density, g./ml. :	(aragonite) 2.93 (calcite) 2.711	1
Coefficient of Thermal Expansion,		
cubical, marble :	$0.3-0.6 \times 10^{-4}$	1
Iceland Spar, 50-60°C :	0.1447×10^{-4}	1
calcite, linear — parallel to axis, 0-85°C :	25.14×10^{-6}	1
perpendicular to axis, 0-85°C :	5.88×10^{-6}	
Heat of Formation, Kcal./mole at 298°K :	aragonite (c) -288.49 calcite (c) -288.45	1, 9
Free Energy of Formation, Kcal./mole at 298°K :	aragonite (c) -269.53 calcite (c) -269.78	1, 9
Entropy, cal./deg./mole at 298°K :	(aragonite) 22.2 ± 0.3 (calcite) 22.2 ± 0.2	3 3
See Tables a and b		
Melting Point:	(aragonite) about 1098°K (825°C) (calcite) 1612°K (1339°C)	1
(at 102.5 atm.)		
Heat of Fusion, 15°g. cal./mole :	12,700	7
Boiling Point :	—	
Transition Point :	—	
Heat of Sublimation :	—	
Heat Content or Enthalpy:	see below	

a. HEAT CONTENT AND **ENTROPY** OF CaCO_3 (**CALCITE**)

(Base, crystals at 298.15°K; mol. wt., 100.09)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	2220	6.38	900	15,500	27.61
500	4610	11.71	1000	18,430	30.70
600	7200	16.13	1100	21,450	33.58
700	9890	20.57	1200	24,550	36.27
800	12,600	24.27			

Calcium Carbonate (page 2)

CaCO₃ (calcite) :

Enthalpy : $H_T - H_{298.15} = 24.98T + 2.62 \times 10^{-3}T^2 + 6.20 \times 10^{-5}T^3 - 9760$
(0.3 percent; 298° - 1200°K)

Heat Capacity : $C_p = 24.98 + 5.24 \times 10^{-3}T - 6.20 \times 10^{-5}T^2$

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
350	1050	3.24	500	4400	11.27
400	2130	6.13	550	5650	13.58
450	3260	8.79	600	6900	15.75

CaCO₃ (aragonite) :

Enthalpy : $H_T - H_{298.15} = 20.13T + 5.12 \times 10^{-3}T^2 + 3.34 \times 10^{-5}T^3 - 7577$
(0.1 percent; 298° - 600°K)

Heat Capacity : $C_p = 20.13 + 20.24 \times 10^{-3}T - 3.34 \times 10^{-5}T^2$

Heat Capacity, cal./deg./mole : (aragonite) 19.42
(calcite) 19.57

Decomposition Temperature : about 825°C

S. Peltier and C. Duval, Anal. Chim. Acta **1**, 345-347 (1947) states that
CaCO₃ loses CO₂ at 660°C and changes to CaO. See also Addnl. Ref. 1.

Decomposition Products : CaO + CO₂ 54V3

For Dissociation Pressure see Ref. 54V3

$\log P_{atm.} = 11,355/T - 5.388 \log T + 26.238$ 42V7

Vapor Pressure : —

X-Ray Crystallographic Data :

	System	Space Group	a	b	c	Axial Angle	Molecules/ Unit Cell
aragonite:	rhomb.	V _h ⁶	4.94	7.94	5.72		4
calcite :	rhbdr.	D _{3d} ⁶	6.361			a = 46°6'	2

Hygroscopicity : —

Solubility Data: In water: insoluble 29
In water saturated with CO₂ : slightly soluble
In dilute acids: soluble with evolution of
CO₂

Health Hazard : Large doses may cause constipation 29

Calcium Carbonate (page 3)

Safety Classifications:

OSM:	not listed
ICC:	not listed
U.N.:	not listed

Fire and Explosion Hazard:	none

Electrostatic Sensitivity :

Use in Pyrotechnics : CaCO_3 is used as a retardant and antacid. It imparts a yellow-red color to burning compositions.

Additional References :

- 1) "Differential Thermal-Analysis Studies of Ceramic Materials: 1, Characteristic Heat Effects of Some Carbonates", R. M. Gruver, J. Am. Ceram. Soc. 33, 96 (1950)

CALCIUM NITRATE, $\text{Ca}(\text{NO}_3)_2$

(Lime Saltpeter, Lime Nitrate, Nitro Calcite, Norway Saltpeter)

Refs.

1, 11.16

Percent Oxygen :	58.50	
Specification No. :	none	
Molecular Weight :	163.10	
Crystalline Form :	cubic	1
Color :	colorless	1
Density, g./ml. :	(solid) 2.36	1
Coefficient of Thermal Expansion :	—	
Heat of Formation, Kcal./mole at 298°K :	(c) -224.0	1, 9
Free Energy of Formation, Kcal./mole at 298°K :	(c) -177.34	1, 9
Entropy, cal./deg./mole at 298°K :	46.2	1, 4, 9
See table below		
Melting Point:	834°K (561°C)	7 ? 9
Heat of Fusion, Kcal./mole :	5.1	9
Boiling Point:	decomposes	1
Heat of Vaporization :	—	
Transition Point:	—	
Heat of Sublimation :	—	

HEAT CONTENT AND ENTROPY OF $\text{Ca}(\text{NO}_3)_2(\text{c})$

(Base, crystals at 298.15°K; mol. wt., 164.10)

4

$T, ^\circ\text{K}$	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	$T, ^\circ\text{K}$	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	3960	11.42	700	18,410	38.01
500	8340	21.15	800	23,970	45.43
600	13,150	29.91			

$\text{Ca}(\text{NO}_3)_2(\text{c})$:

Enthalpy : $H_T - H_{298.15} = 29.37T + 18.40 \times 10^{-3}T^2 + 4.13 \times 10^{-5}T^3 - 11,778$ (0.3 percent; 298° - 800°K)

Heat Capacity : $C_p = 29.37 + 36.80 \times 10^{-3}T - 4.13 \times 10^{-5}T^2$

Heat Capacity, cal./deg./mole : (solid) 35.69
See also equation immediately above

9

Decomposition Temperature : 480-500°C

Addn. Ref. 1

Decomposition Products :

For DTA and TGA see Refs. 33 and 47

Vapor Pressure :

Calcium Nitrate, $\text{Ca}(\text{NO}_3)_2$ (page 2)

X-Ray Crystallographic Data :

<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>Molecules/Unit Cell</i>	
cubic	T_h	7.60	4	1, 97V7
Hygroscopicity : Deliquesces in moist air. Keep in tightly closed container.				29
Solubility Data: In water, g./100 ml. at °C:				
				102 at 0°, 341 at 25°, 376 at 100°
In acids:				very soluble
In ethyl, acetate, and alcohol :				soluble
Health Hazard : Large amounts taken internally are poisonous.				12
Safety Classifications :				
OSM: Class 1				
ICC : Listed under "Explosives and Other Dangerous Articles." Oxidizing material ; yellow label.				
Fire and Explosion Hazard : $\text{Ca}(\text{NO}_3)_2$ may explode when shocked, or by heat, flame, or chemical reaction. It is a strong oxidizing agent and reacts vigorously with oxidizable materials. $\text{Ca}(\text{NO}_3)_2$ emits toxic fumes on decomposition.				12
Electrostatic Sensitivity :				
Use in Pyrotechnics : $\text{Ca}(\text{NO}_3)_2$ is used as an oxidizer and to impart a yellow-red color to burning compositions.				1
Additional References :				
1) C.A. 49, 12932 (1955)				

CALCIUM OXALATE, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$
(Monohydrate)

Refs.

Specification No.:	JAN-C-628
Molecular Weight:	146.12
Crystalline Form:	monoclinic
Color:	colorless
Density, g./ml.:	(solid) 2.2
Coefficient of Thermal Expansion:	—
Heat of Formation, Kcal./mole at 298°K:	-399.1
Free Energy of Formation, Kcal./mole at 298°K:	-360.6
Entropy, cal./deg./mole at 298°K:	37.28
Melting Point:	loses H_2O at 473° K (200°C)
Heat of Fusion:	—
Boiling Point:	—
Transition Point:	—
Heat of Sublimation:	—
Heat Content or Enthalpy:	—
Heat Capacity, cal./deg./mole:	(solid) 36.40
Decomposition Temperature :TGA	

1, 5

1

1

1

1

1, 9

1, 29

9

Addnl. Refs.
1, 2, 3, 4, 5

See pyrolysis curve below

Decomposition Products : Calcium carbonate, calcium oxide.

91

See pyrolysis curve below

Dissociation Pressure for CaC_2O_4 :

91

T°C	P _{mm.}	T°C	P _{mm.}
378	8.2	410	250.0
388	80.0	416	587.0
403	134.0	418	684.0

X-Ray Crystallographic Data:

System	Space Group	a	c	Molecules/Unit Cell
$2\frac{1}{2} \text{H}_2\text{O}$ tetragonal	C_{4h}	12.302	7.381	
$3 \text{H}_2\text{O}$	C_{2h}	12.376	7.377	4

18V2

85

Hygroscopicity:

Solubility Data:

In water, acetic acid, and alcohol:	insoluble
in acids:	soluble

1

Health Hazard : Corrosive and produces local irritation. Has a caustic effect on mouth, esophagus. and stomach. Can cause severe damage to kidneys.

12

Calcium Oxalate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (page 2)

Safety Classifications:

OSM : not listed

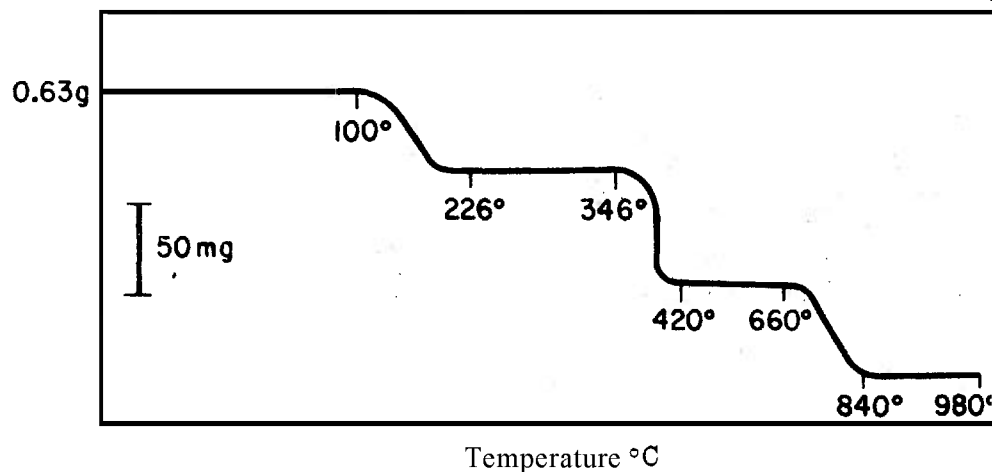
ICC: not listed

Fires and Explosion Hazard: Can be dangerous when heated to decomposition because of toxic fumes. 12

Electrostatic Sensitivity : —

Pyrolysis Curves of Calcium Oxalate, Carbonate, and Oxide

Addnl. Ref. 1



Use in Pyrotechnics: As a retardant and to impart a pink color to burning compositions.

Additional References:

- 1) "On the Thermogravimetry of Analytical Precipitates," S. Peltier and C. Duval, *Anal. Chim. Acta* **1,347** (1947)
- 2) E. S. Freeman and B. Carroll, *J. Phys. Chem.* **65,394** (1958)
- 3) *Nature* **178,324** (1956)
- 4) "Anhydrous Calcium Oxalate as a Weighing Form for Calcium," C. C. Miller, *Analyst* **78, 186** (1953)
- 5) *C.A.* **47, 5756** (1953)

CALCIUM OXIDE, CaO

Refs.

(Lime, Burnt Lime, Fat Lime, Quick Lime, Calx, Calcia)

Specification No. :

Molecular Weight :

56.08

Crystalline Form :

cubic

Color :

colorless

Density, g./ml. :

3.346

Coefficient of Thermal Expansion, cubical :

5.0×10^{-7}

Heat of Formation, Kcal./mole at 298°K :

(c) -151.9

See Table a

Free Energy of Formation, Kcal./mole at 298°K : (c) -144.4

See Table a

a. HEAT AND FREE ENERGY OF FORMATION OF CaO (c)

T, °K	H (cal./mole)	F° (cal./mole)
298.16	-150,650 (± 400)	-143,250 (± 500)
400	-150,600	-140,600
500	-150,500	-138,250
600	-150,450	-135,800
673	-150,400	-134,000
673	-150,500	-134,000
700	-150,450	-133,350
800	-150,400	-130,900
900	-150,300	-128,500
1000	-150,250	-126,050
1100	-150,200	-123,600
1124	-150,200	-123,050
1124	-152,450	-123,060
1200	-152,350	-121,050
1300	-152,200	-118,450
1400	-152,100	-115,850
1500	-151,950	-113,300
1600	-151,800	-110,700
1700	-151,650	-108,150
1760	-151,550	-106,650
1760	-188,150	-106,660
1800	-188,000	-104,800
1900	-187,550	-100,200
2000	-187,150	-95,550

Phase Changes of Metal

T.P., **673°K** ; $\Delta H = 115 \text{ cal./g.-atom}$

M.P., 1124°K ; $\Delta H = 2230 \text{ cal./g.-atom}$

B.P., 1760°K ; $\Delta H = 36,600 \text{ cal./g.-atom}$

Calcium Oxide, CaO (page 2)

Free Energy Equations :

Reaction	Range of Validity, °K
1) $\text{Ca } (\alpha) + \frac{1}{2} \text{O}_2 (\text{g}) = \text{CaO } (\text{c})$ $\Delta F_T^\circ = -151,850 - 6.56T \log T + 1.46 \times 10^{-3}T^2 + 0.68 \times 10^5T^{-1} + 43,931'$	298.16 to 673
2) $\text{Ca } (\beta) + \frac{1}{2} \text{O}_2 (\text{g}) = \text{CaO } (\text{c})$ $\Delta F_T^\circ = -151,730 - 4.14T \log T + 0.41 \times 10^{-3}T^2 + 0.68 \times 10^5T^{-1} + 37.63T$	673 to 1124
3) $\text{Ca } (\text{l}) + \frac{1}{2} \text{O}_2 (\text{g}) = \text{CaO } (\text{c})$ $\Delta F_T^\circ = -153,480 - 1.36T \log T - 0.29 \times 10^{-3}T^2 + 0.68 \times 10^5T^{-1} + 31.49T$	1124 to 1760
4) $\text{Ca } (\text{g}) + \frac{1}{2} \text{O}_2 (\text{g}) = \text{CaO } (\text{c})$ $\Delta F_T^\circ = -194,670 - 718T \log T - 0.29 \times 10^{-3}T^2 + 0.68 \times 10^5T^{-1} + 73.84T$	1760 to 2000
Entropy, cal./deg./mole at 298°K :	(c) 9.5 (gas) 52.3

See Table b

b. HEAT CONTENT AND ENTROPY OF CaO (c) (Base, crystals at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	1100	3.17	1300	12,110	17.38
500	2230	5.69	1400	13,430	18.36
600	3400	7.82	1500	14,760	19.28
700	4600	9.67	1600	16,100	20.14
800	5820	11.30	1700	17,440	20.96
900	7040	12.73	1800	18,780	21.72
1000	8270	14.03	1900	20,130	22.45
1100	9520	15.22	2000	21,480	23.15
1200	10,800	16.34			

CaO (c) :

Enthalpy : $H_T - H_{298.15} = 11,67T + 0.54 \times 10^{-3}T^2 + 1.56 \times 10^5T^{-1} - 4051$
(0.3 percent ; 298-2000°K)

Heat Capacity: $C_p = 11.67 + 1.08 \times 10^{-3}T - 1.56 \times 10^5T^{-2}$

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	825	2.38	1000	6005	10.25
500	1665	4.25	1200	7775	11.87
600	2515	5.80	1400	9545	13.23
700	3380	7.13	1600	11,325	14.42
800	4250	8.30	1800	13,115	15.47
900	5125	9.33	2000	14,910	16.42

Calcium Oxide, CaO (page 3)

Enthalpy: $H_f - H_{298.15} = 8.70T + 0.68 \times 10^{-3}T^2 + 0.74 \times 10^{-6}T^3 - 2849$ (0.2percent; 298° - 2000°K)		CaO(g) :	
Heat Capacity : $C_p = 8.70 + 0.16 \times 10^{-3}T - 0.74 \times 10^{-6}T^2$			
Melting Point :		2843°K (2570°C)	31A
Heat of Fusion, Kcal./mole :		12	9
Boiling Point:		3123°K (2850°C)	31A
Heat of Vaporization :		—	
Transition Point :		—	
Heat of Sublimation :		—	
Heat Capacity, cal./deg./mole :		(solid) 10.23	9
See also equations under Tables b and c			
Decomposition Temperature and Products :		—	
Dissociation Pressure : $\log_{10} P_{mm} = 2.74/10^4 T + 9.97$ (over the temperature range, 1600–1750°K)			Addnl. Ref. 2
See also Refs. 42V7 and 44B2 for additional values			
X-Ray Crystallographic Data :			
System cubic	Space Group O_h	a 4.797	Molecules/Unit Cell 4
Hygroscopicity : Very hygroscopic. Combines with water to form Ca (OH) ₂ . Keep containers dry and tightly closed.			1 29
Solubility Data : In water, 0.131 at 10°C : 0.07 at 80°C :			1
In acids, glycerol :		reacts to form Ca (OH) ₂	
In alcohol :		soluble	
		insoluble	
Health Hazard: Caustic reaction on skin and respiratory system. The dust is an industrial hazard. Causes dermatitis. Treat with large quantities of water.			12, 25, 29
Safety Classifications :			
OSM :		not listed	
ICC :		not listed	
U.N. :		corrosive	
Fire and Explosion Hazard : Slightly dangerous. Produces heat on contact with water, steam, acids, or acid fumes.			12
Electrostatic Sensitivity :		—	
Use in Pyrotechnics: Calcium oxide is a product of high temperature burning of calcium and many of its compounds.			
Additional References :			
1) Ref. 64			
2j "Vapor Pressure Determination of BaO, SrO and CaO, and Their Mix- tures from Measurements of the Rate of Evaporation," A. Claassen and C. Veenemans, Zeit. Physik 80, 342 (1933); cited by Ref. 65			

CALCIUM PERCHLORATE (ANHYDROUS) , $\text{Ca}(\text{ClO}_4)_2$

Refs.

Percent Oxygen :	53.56				
Specification No. :	_____				
Molecular Weight :	238.99				
Crystalline Form :	cubic	1			
Color :	colorless	1			
Density, g./ml. :	_____				
Coefficient of Thermal Expansion :	_____				
Heat of Formation, Kcal./mole at 298°K :	(estd.) -178	72			
Free Energy of Formation:	_____				
Entropy :	_____				
Melting Point :	396°K (123°C)	65			
Heat of Fusion :	_____				
Bailing Point':	decomposes	65			
Values in the literature range from less than 573°K (300°C) to about 683°K (410°C)					
Transition Point:	_____				
Heat of Sublimation :	_____				
Heat Content of Enthalpy:	_____				
Heat Capacity:	_____				
Decomposition Temperature :	bubbling slight at 258°C , vigorous at 285°C	47			
DTA and TGA, see Refs. 33, 47					
Decomposition Products :	CaCl₂ + O₂ with traces of CaO and Cl ₂	Addnl. Ref. 1			
Vapor Pressure :	_____				
X-Ray Crystallographic Data for Ca(ClO ₄) ₂ •3H ₂ O :					
<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>c</i>	<i>Molecules/Unit Cell</i>	
hexagonal	C _{6v} ⁴	7.71	5.42	2	65
Hygroscopicity :				deliquescent	1
Solubility Data : In water :				188.6 g./100 g. at 25°C very soluble in hot water	1
Solubility in Organic Solvents at 25°C :					65, 72, 77
	<i>Solvent</i>	<i>g./100 g. solvent</i>			
	acetone	61.76			
	ethyl acetate	113.5			
	ethyl alcohol	166.2			
	ethyl ether	0.26			
	methyl alcohol	237.4			

Galcium Perchlorate (Anhydrous), $\text{Ca}(\text{ClO}_4)_2$ (page 2)

Health Hazard: CaClO_4 is a moderate irritant to the skin and mucous membranes. Avoid contact with skin. A weak muscular poison. It is not cumulative and not reduced in the body. 12, 65

Safety Classifications:

OSM: Class 1. Class 2 when not packed in original containers or equivalent.

ICC: Oxidizing material; yellow label. Listed under "Explosives and Other Dangerous Articles."

Fire and Explosion Hazard: CaClO_4 is a powerful oxidizer. It may cause fires or explosions when shocked or heated or by chemical action with reducing substances such as carbonaceous materials. It forms explosive mixtures with sulphur, powdered magnesium, and aluminum. It also emits highly toxic fumes when heated. 12

Electrostatic Sensitivity :

Use in Pyrotechnics: CaClO_4 is used as an oxidizer and to impart a yellow-red color to burning compositions.

Additional References:

- 1) C.A. 51, 2439 (1957)

CALCIUM PHOSPHIDE, Ca_3P_2
(Photophor)

Refs.

Specification No.:

MIL-C-3539

The specification covers two types: Type A, uncoated, and Type B, coated with $\text{K}_2\text{Cr}_2\text{O}_7$. Both types are in the form of solid sticks or lumps $\frac{1}{4}$ to 1 in. in diameter. The types differ in their rate of reaction with water. When immersed in sea water, Type A shall immediately produce a vigorous reaction with a strong bright flame while Type B is required to give a maximum evolution of smoke and flames at approximately 15 min. after contact with the water. The two types also evolve different amounts of gas for equal masses.

Molecular Weight :	182.20	
Crystalline Form :	cubic	Addnl. Ref. 2
Color :	redish-brown,	Addnl. Ref. 2
Density, g./ml. :	(solid) 2.51 at 15°C	3A
Coefficient of Thermal Expansion :	—	
Heat of Formation, Kcal./mole at 298°K :	(c) -120.5	1, 9
Free Energy of Formation :	—	
Entropy :	—	
Melting Point :	about 1873°K (1600°C)	1, 29
Heat of Fusion:	—	
Boiling Point:	—	
Transition Point :	—	
Heat of Sublimation :	—	
Heat Content or Enthalpy:	—	
Heat Capacity :	—	
Decomposition Temperature:	Can be heated to 1250°C without decomposing but reacts with moist air. Reacts in air about 300°C and becomes incandescent.	Addnl. Ref. 1, 54V8
Decomposition Products :	—	
Vapor Pressure :	—	
X-Ray Crystallographic Data :	—	
Hygroscopicity :	Decomposed on contact with water, evolving spontaneously flammable phosphine.	29, Spec.
Solubility Data :	In water : see Hygroscopicity above	
	In acids: soluble	1
	In alcohol, ether, benzene : insoluble	
Health Hazard :	Dangerous, due to reactivity with water which evolves severely toxic phosphine.	12, 93
Safety Classifications :		
OSM :	not listed	
ICC:	Flammable solid ; yellow label. Listed under "Explosives and Other Dangerous Materials."	

Calcium Phosphide, Ca_3P_2 (page 2)

Fire and Explosion Hazard : Liable to spontaneous combustion. Dangerous when heated as it emits highly toxic fumes of oxides of phosphorus. May explode when heated by a flame. See Hygroscopicity.

Caution: Keep dry and tightly closed (for this reason it is packaged in soldered tins). Under these conditions no gas should be evolved.

Electrostatic Sensitivity : _____

Use in Pyrotechnics : As a fuel and to impart a yellow-red color to burning compositions or to produce smoke and flame.

Additional References :

- 1) "Phosphorus and Its Compounds," by V. Waser, Interscience Publishers, Inc., New York (1958)
- 2) M. V. Stackelberg and R. Paulus, *Zeit. Physik. Chem.* 22B, 305 (1933)

15, 12,
Addnl. Ref. 1

29, spec.

Refs.

2 50V2

12
1

Addnl. Ref. 1

32 (Table 14)

Time	65% R.H.		75% R.H.		86% R.H.		93% R.H.	
	Stat.	Vac.	Stat.	Vac.	Stat.	Vac.	Stat.	Vac.
24 hrs.	14.0	8.3	11.5	14.1	25.4	19.0	27.1	23.4
1 week	12.8	12.1	13.0	12.5	23.2	25.6	23.9	27.5
30 days			14.1		27.7		30.9	

Solubility Data :

soluble in petroleum
solvents

50

Calcium Resinate (page 2)

Health Hazard :	unknown	12
Safety Classification :		
OSM :	not listed	
ICC :	Flammable solid :yellow label. Listed under "Explosives and Other Dangerous Materials."	
Fire and Explosion Hazard:	Slight; when heated it can react with oxidizing materials.	17
Electrostatic Sensitivity :	—	
Use In Pyrotechnics :	Calcium resinate is used as a retardant fuel, and binding agent. Imparts a yellow-red color to burning compositions. Use also as a waterproofing agent.	
Additional References :		
1)	"A Comparative Study of the X-Ray Diffraction Patterns and Thermal Transitions of Metal Soaps," M. J. Vold and R. D. Vold, J. Am. Oil Chemists' Soc. 26,520 (1949)	

CALCIUM SILICIDE, CaSi_2

Refs.

Specification No. :

JAN-C-324

The specification covers two grades which differ in purity and granulation. Grade I is used in smoke mixtures, and Grade II in both smoke mixtures and tracer compositions.

Molecular Weight :

96.26

Crystalline Form :

glassy solid

1

Color :

—

Density, g./ml. :

(solid) 2.5

1

Coefficient of Thermal Expansion :

—

Heat of Formation, Kcal./mole at 298°K :

(c) -36

1, 9

Free Energy of Formation :

—

Entropy :

—

Melting Point:

1493°K (1220°C)
1020°C

9
44, Addnl.
Ref. 2

Heat of Fusion:

—

Boiling Point :

—

Transition Point.:

—

Heat of Sublimation :

—

Heat Content or Enthalpy :

—

Heat Capacity :

—

Decomposition Temperature :

Decomposition Products :

Vapor Pressure :

—

X-Ray Crystallographic Data :

System	Space Group	a	Axial Angle	Molecules/Unit Cell
hexagonal	D_{3d}^2	10.4	21°30'	2

1

Note: The structure is characterized by layers of rings with six Si atoms

Addnl. Refs.
2, 3

Hygroscopicity : See Solubility (in water)

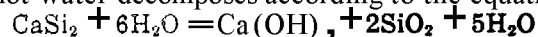
Solubility Data : In cold water :

insoluble

1

In hot water decomposes according to the equation :

Addnl. Ref. 2



In acids and bases:

decomposes

Health Hazard : Has caustic action irritating to the skin and respiratory system

12

May cause dermatitis and irritation to the eyes and mucous membranes.

(Treatment — wash with large volumes of water)

Believed to be nontoxic.

93

Calcium Silicide, CaSi_2 (page 2)

Safety Classification :

OSM : not listed
ICC : flammable solid

Fire and Explosion Hazard : **Dangerous** by chemical reaction with oxidizers. When heated can burn or explode and emit toxic fumes. In contact with water may emit flammable silicon hydrides.

12, Addnl.
Ref. 1

Electrostatic Sensitivity : ———

Use in Pyrotechnics: CaSi_2 is **used** as a fuel and **to** impart a yellow-red color to burning compositions. **Used** in igniter compositions for tracer projectiles.

17, Addnl.
Ref. 4

Additional References :

- 1) E. Wöhler and E. Schiephake, **Zeit. anorg. Chem.** **151**, 1 (1926)
- 2) "Silicon and Its Binary **System**," A. S. Birezhnoi (Translated from the Russian), Consultants Bureau, New York (1960)
- 3) H. Bohm and O. Hassel, **Zeit. anorg. Chem.** **160**, 162 (1927)
- 4) C.A. **49**, 14326 (1955)

CALCIUM STEARATE

Formula :	$\text{Ca}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$	
Specification No. :	JAN-C-263	
Molecular Weight :	607.00	
Crystalline Form :	crystalline powder	
See Addnl. Refs. 2, 3		
Color :	opaque, translucent after heating and cooling	Addnl. Ref. 4
Density :	—	
Coefficient of Thermal Expansion :	—	
Heat of Formation, Kcal./mole at 18°C :	$H_f = -662.6$ $H_v = -641.1$	Addnl. Ref. 1
Free Energy of Formation:	—	
Entropy :	—	
Melting Point:	452–453°K (179–180°C)	1
Heat of Fusion :	—	
Boiling Point:	decomposes	1
Transition Point: Phase changes at 65, 86, 123, 150, 195 and 350°C . Below 150°C the stable phases are crystalline.		Addnl. Refs. 2, 3
Transition Temperatures and Heats of Transition		
°C	cal./mole	
89		
107	9080	
152		
190		
58		
89		
106	7430	
146		
187		
Note: Values vary with the source of the samples, which are not pure.		
The 150–195°C phase is a liquid crystal. Quenching from a temperature of 123–150°C produces an unstable crystal, but an unstable vitreous form results on quenching from above 150°C . Technical Ca stearate resembles the pure material but assumes the vitreous form more readily and crystallizes with difficulty.		Addnl. Ref. 2
Heat of Sublimation :	—	
Heat Content or Enthalpy:	—	
Heat Capacity:	—	
Decomposition Temperature, °C :	above 350	Addnl. Refs. 2, 3, 4
For DTA see Addnl. Ref. 4		

Calcium Stearate (page 2)

Decomposition Products : _____

Vapor Pressure : _____

X-Ray Crystallographic Data :

For X-Ray Diffraction Data see Addnl. Ref. 5

Hygroscopicity : _____

Solubility Data: In water:

0.004 g./100 ml. at 15°C
(not readily wetted)

1

In alcohol and ether:

insoluble

In methyl alcohol and toluol, g./100 g. :

Temp. °C	methyl alcohol	toluol
25	0.05	0.03
50	0.09	0.47
75		0.22
100		gelled*

Addnl. Ref. 6

*Ca stearate precipitated on cooling

Health Hazard:

none mentioned

Safety Classifications:

OSM:

not listed

ICC:

not listed

Fire and Explosion Hazard :

Electrostatic Sensitivity:

Use in Pyrotechnics : As a fuel and to impart a yellow-red color to burning compositions. Also waterproofing, lubricating, and bonding agent.

Additional References :

- 1) E. Médard, *Mém. artillerie franç* **28, 467 (1954)**
- 2) "Polymorphic Transformations of Ca Stearate and Ca Stearate Monohydrate," R. Vold et al., *J. Colloid. Sci.* **3, 339 (1948)**
- 3) "Crystal Forms of Anhydrous Ca Stearate Derivable from Calcium Stearate Monohydrate," M. Vold et al., *J. Colloid Sci.* **4, 93 (1949)**
- 4) "Differential Thermal Analysis of Metal Soaps," G. Hattiangdi et al., *Ind. Eng. Chem.* **41, 2320 (1949)**
- 5) "Characterization of Heavy Metal Soaps by X-Ray Diffraction," R. Vold and G. Hattiangdi, *Ind. Eng. Chem.* **41, 2311 (1949)**
- 6) "Aero Metallic Stearates," Am. Cyanamid Co., Bound Brook, N. J. (1960)

CARBON BLACK (DRY) and LAMPBLACK, C
(Cape Cod Black, Gloss Soot, Light Soot, Flame Soot,
Flame Black, Furnace Black, Channel Black, and a wide
variety of proprietary namee and numbers)

Specification No. : Carbon black (dry) : MILC-11403
 Lampblack : TT-L-706

Carbon black is an amorphous, quasi-graphitic carbon obtained by burning gas, oils, tars, or other carbonaceous material in an insufficient amount of air to form a deposit of soot. By varying the process and the starting material, properties of the products can be varied considerably. Carbon black is usually one of the following types :

- a) Animal charcoal, made by charring bones, meat, or blood.
- b) Gas black, furnace black, or channel black, made by the incomplete combustion of natural gas.
- c) Lampblack obtained by burning various fats, oils, and resins, under controlled conditions.
- d) ~~Wood~~ and vegetable charcoals.

Carbon blacks are very finely divided. Most individual particles are in the range of 13 to 274 m μ . As colloids, the particles are negatively charged and show the Brownian movement. Lampblack is amorphous but most carbon blacks are a mixture of the amorphous and crystalline forms. Carbon blacks have an enormous surface per unit mass and are very absorbent. The structure and pH can also be varied over a wide range. Carbon blacks thus find a wide variety of uses.

The individual fine particles are composed of several thousand crystallites. These are in parallel layers of carbon atoms arranged in hexagonal rings as in graphite, but in carbon black the symmetry is much less precise so that the carbon atoms in adjacent layers are rotated about an axis at right angles to their plane. The structure is similar to that of true graphite as the carbon rings are arranged roughly parallel and equidistant but otherwise completely random, and the dimensions within a layer are the same as in graphite. The layer is somewhat larger than in graphite. The effect of heat treatment is to increase the size of the parallel layer groups. On graphitization the material changes discontinually to the crystalline graphite structure. The usual carbon black is not finely divided graphite. Small angle scattering indicates the existence of clusters of a few hundred angstrom units in size. These clusters are measured by microscope units, by the electron microscope and by surface areas, rather than the much smaller parallel layer groups.

Molecular Weight:	12.011	
Crystalline Form :	fluffy, amorphous powder	1
Color:	black	1
Density, g./ml.:	(solid) 1.8-2.1	1

Refs.

16, 22, 29,
50V3

Addnl. Refs.
4, 5, 6, 10, 11

Carbon Black, C (page 2)

Coefficient of Thermal Expansion, linear :	0.65 × 10 ⁻⁶	Addnl. Ref. 1
see also Ref. 63		
Heat of Formation:	—	
Free Energy of Formation:	—	
Entropy :	—	
Melting Point:	3925–3970°K, sublimes (3652–3697°C)	1
Heat of Fusion:	—	
Boiling Point :	4473°K (4200°C)	1
Heat of Vaporization, cal./g. :	11,900	Addnl. Ref. 1
Transition Point:	—	
Heat of Sublimation, Kcal./mole :	135.7 133 ± 12	Addnl. Ref. 7 Addnl. Ref. 3
Heat Content or Enthalpy:	—	
Heat Capacity:	—	
Decomposition Temperature:	—	
Decomposition Products:	—	
Vapor Pressure :	—	

Press. mm.	04	20	120	240	760	Addnl. Ref. 8	
Temp. °C	2375	2935	3250	3490	3700		
Press. mm.	243	327	380	509	608	760	Addnl. Ref. 9
Temp. °C	4015	4052	4801	4117	4137	4190	

X-Ray Crystallographic Data :

See Addnl. Refs. 3, 4, 10, 11

Hygroscopicity :

Solubility Data : In water, acids, and alkalies : insoluble

Health Hazard : Considered nontoxic. Prolonged internal use may cause vitamin and mineral deficiency and interfere with digestion.

Safety Classifications :

OSM : Atmospheres containing carbon black are included under hazardous locations, class 11.

ICC : not listed

Fire and Explosion Hazard: Slight when exposed to heat or flame. Lampblack made by incomplete combustion of petroleum may heat spontaneously when freshly bagged. It has great affinity for liquids and heats spontaneously on contact with drying oils. It should be thoroughly cooled before bagging and stored in a cool, dry place away from oxidizing materials. Lampblack dust can be exploded. See data following:

Carbon Black, C (page 3)

Explosibility of Lampblack :

<i>Concentration</i>	<i>Max. Press.</i>	<i>Avg. Rate of Press. Rise</i>	<i>Max. Rate of Press. Rise</i>	86
(mg./l.)	(lbs./sq. in.)	(lbs./sq. in./sec.)	(lbs./sq. in./sec.)	
100	10	13	119	

Ignition Temperature, °C :

Carbon black (produced in reducing atmosphere) 535

Thermal carbon blacks : 449-485

Lampblack (oxidizing atmosphere) : 352-362

Carbon blacks (natural gas) : 313-324

Heat of Combustion (at constant volume), cal./g. :

Carbon amorphous : 8130

Carbon black (dried at 100°C) : 7810

(degassed at 1000°C) : 8270

Specific Heat at 25°C, g./cal./g. 0.2

Use in Pyrotechnics: Lampblack is used by the Chemical Corps as a pigment in protective coatings.

Additional References:

- 1) "Industrial Carbon," C. L. Mantell, D. Van Nostrand Co., Inc., Princeton, N. J. (1946)
- 2) L. Médard, Mém. artillerie franç, **28, 485 (1954)**
- 3j "Ionization and Dissociation by **Electron** Impact, Methylene, Methyl and **Methane**," A. Langer et al., J. Chem. **Phys. 22**, 1836 (1954)
- 43 **Chem. Eng. News** 23, 2078 (1945)
- 5) "Carbon Black," E. Cohan and H. Cohan, Vol. **5**, pt 11, "The Science of Petroleum," B. T. Brooks and A. E. Dunstan, **Eds.**, Oxford University Press, New York (1953)
- 6) J. D. Bernal, Proc. Royal Soc. **106A, 749 (1924)**
- 7) **E. Lindholm, C.A. 51, 6345 (1957)**
- 8) **A. Thiel and F. Ritter, Zeit. anorg. Chem. 132, 125, 153 (1923)**
- 9) **H. Kohn, Zeit, Physik 3, 143 (1920)**
- B0) "An X-Ray Study of Carbon Black," J. Biscoe and B. E. Warren, J. **Appl. Phys. 23, 364 (1942)**
- 11) "X-Ray Study of Carbon Black," B. E. Warren, J. Chem. Phys. **2, 551 (1934)**

Addnl. Ref. 1

Addnl. Ref. 2

Addnl. Ref. 1

CARBON TETRACHLORIDE, CCl₄
(Tetrachloromethane, Benzinoform)

Refs.

Specification No.:	O-C-141	1, 11
Marking: The Air Force requires that each package bear a label as follows: "Caution: Volatile poisonous solvent. Use with adequate ventilation. Avoid prolonged breathing of vapor. Avoid contact with skin."		
Molecular Weight:	153.84	
Normal Color and Form:	colorless liquid	1
Density, g./ml.:	(liquid) 1.595 at 20/4 1.63195 at 0/4°C	1
Coefficient of Thermal Expansion, cubical, 0-76°C:	1.236×10^{-3}	1, 3
$V_t = V_0 + 1.8384t^{-3} + 0.89881t^{-6} + 1.35135 \times 10^{-9}$		
Heat of Formation, Kcal./mole at 298°K:	(gas) -25.5 (liquid) -33.3	1, 9
Free Energy of Formation, Kcal./mole at 298°K:	(gas) -15.3 (liquid) -16.4	1, 9
Entropy, cal./deg./mole at 298°K:	(gas) 73.95 (liquid) 51.25	1, 9 .
<i>See table below</i>		
Melting Point:	250.3°K (-22.8°C)	9
Heat of Fusion, Kcal./mole:	0.60	9
Boiling Point:	349.9°K (76.8°C)	9
Heat of Vaporization, Kcal./mole:	7.17	9
Transition Point:	225.5°K (-47.6°C)	9
Heat of Transition, Kcal./mole:	1.09	9
Heat of Sublimation:	—	

HEAT CONTENT AND ENTROPY OF CCl₄(g)
(Base, ideal gas at 298.15°K)

4

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	2140	6.16	1000	16,570	27.99
500	4395	11.19	1100	19,080	30.38
600	6740	15.46	1200	21,610	32.58
700	9150	19.17	1300	24,140	34.61
800	11,600	22.45	1400	26,680	36.49
900	14,080	25.37	1500	29,220	38.24

Carbon Tetrachloride, CCl₄ (page 2)

CCl ₄ (g) :							
Enthalpy : $H_T - H_{298.15} = 24.17T + 0.60 \times 10^{-3}T^2 + 4.10 \times 10^5T^{-1} - 8635$							4
(0.3 percent ; 298° - 1500°K)							
Heat Capacity : $C_p = 24.17 + 1.20 \times 10^{-3}T - 4.10 \times 10^5T^{-2}$							
Heat Capacity, cal./deg./mole :					(liquid) 31.47		4, 9
					(gas) 19.96		
Decomposition Temperature : Noticeable at 150°C particularly in the presence of Cl acceptors, e.g., metals and metal oxides.							Addnl. Refs. 2, 3, 4
Decomposition Products : Phosgene may be formed, especially in the presence of metals.							
Vapor Pressure :							1
Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	-50.0	-19.6	+4.2	23.0	57.8	76.7	-22.6
X-Ray Crystallographic Data :							
Interatomic Distances and Molecular Configuration :							
C-Cl, 1.76Å ± 0.01 ; Cl-Cl, 2.86 ± .01							
Tetrahedral model confirmed spectroscopically							
Hygroscopicity :							
Solubility Data : Solubility of water in CCl ₄ is 0.008% by weight at 20°C. Solubility in water, 0.8 g./100 ml. at 20°C. CCl ₄ is miscible in all proportions with alcohol, ether, chloroform, benzene, halogenated hydrocarbons, and most solvents.							53V1
Health Hazard : CCl ₄ is a systemic poison with a narcotic action resembling that of chloroform. It may cause death through respiratory failure, and can cause serious effects to kidneys, liver, lungs, and the nervous system. It can be fatal when taken internally. Dermatitis may result from repeated skin contact, and its vapors are toxic.							12, 14, 29
M.A.C.: 25 parts per million in air for an 8-hr. work day.							
Caution: Do not use CCl ₄ to fight fire in unventilated spaces such as small rooms or closets. Store in airtight drums.							
Note: CCl ₄ poisoning is detectable in the blood and urine.							
Safety Classifications :							
OSM:				not listed			
ICC:				not listed			
Fire and Explosion Hazard : CCl ₄ is not combustible, but its vapor is toxic. It is dangerous when heated to decomposition due to formation of highly toxic phosgene.							12, 14, 29
Electrostatic Sensitivity: —							
Azeotrope: CCl ₄ forms an azeotrope with water which boils at 66°C at 1 atm. and contains 4.1 % water.							53V2

Carbon Tetrachloride, CCl₄ (page 3)

Use in Pyrotechnics: CCl₄ is used as a noncombustible solvent and fire retardant in certain compositions.

Additional References :

- 1) Ref. 52
- 2) "Poisonous Gases from Carbon Tetrachloride Fire Extinguishers," A. C. Fieldner et al., J. Franklin Inst. 190, 543 (1920)
- 3) "Determination of Phosgene," A. C. Fieldner et al., Ind. Eng. Chem. Anal. Ed. 8, 20 (1936)
- 4) "Mass Spectrographic Study of the Species CS, SO, and CCl₂ Produced in Primary Heterogeneous Reactions," L. P. Blanchard and P. LeGoff, Can. J. Chem. 35, 89 (1957)

CASTOR OIL		Refs.
(Ricinus Oil, Oil of Palma Christi, Tangan-Tangan Oil, Ricinus Communis)		1, 29
Formula : Castor oil is a natural product of somewhat variable composition.		
Specification No. :	MIL-C-15179A (dehydrated)	
Castor oil is a light yellow to brownish oil obtained from the seed beans of the castor plant. When pure and fresh, it is nearly colorless and transparent. The hot pressed oil is brownish. Castor oil does not readily turn rancid, and is classed as a non-drying oil.		
Dehydrated castor oil must be made by the dehydration of castor oil and polymerization of the resulting product, without admixture of other oils.		
Molecular Weight :	castor oil is a variable natural product	
Normal Color and Form:	pale yellow oil	29
Density, g./ml. : :	(liquid) 0.960-967	1
Coefficient of Thermal Expansion :	—	
Melting Point:	turbid at 261°K (-12°C), solid at 255-256°K (-17 to -18°C)	1
Boiling Point:	586°K (313°C)	12
Decomposition Temperature:	—	
Decomposition Products :	—	
Vapor Pressure:	—	
Hygroscopicity :	—	
Solubility Data :	Miscible with absolute ethyl alcohol, methanol, ether, chloroform, glacial acetic acid.	29
Health Hazard :	slight, used medicinally	
Safety Classifications :		
OSM:	not listed	
ICC :	not listed	
Fire and Explosion Hazard:	combustible	
Flash Point, °F:	445 (closed cup) ; 545 (open cup)	75
Autoignition Temperature, °F :	905	75
To fight fire:	use foam, dry chemical, CCl ₄ or water	95
Electrostatic Sensitivity :	—	
Use in Pyrotechnics :	Castor oil is used as a fuel, as a waterproofing and binding agent, and to reduce sensitivity to friction.	17
See Addnl. Refs.		

Castor Oil (page 2)

Castor oil composition, %:

diglycerides of ricineleic acid:	80-86
oleic acid:	7-9
linoleic acid:	3-3.5
stearic acid:	0.3
dihydrostearic acid:	0.6-1.8
tocophorol:	about 0.05

Castor oil is dextro rotary and has the following characteristics:

Refractive index: $n_D^{20} = 1.473-1.477$
 $n_D^{25} = 1.466-1.473$

Viscosity at **25°C**, poises: **6-8**

Surface tension at 20°C, dynes/cm.: 39.0

80°C, dynes/cm.: 35.2

Acid value: **0.12-0.8**

Saponification value: **175-183**

Iodine value (Wijs): **84**

Reichert Meissl number: **1.4**

Maumené number: **46-47**

Acetyl value: **146-150.5**

Unsaponifiable matter: 0.6

Specific heat, cal./g., at 40°C: **0.52**

at 200°C: **0.59**

Additional References:

- 1) "Explosives, Matches, and Fireworks," J. Reilly, **The University Press**
Cambridge, England (1938)
- 2) "Fats and Oils," H. G. Kirschenbauer, Reinhold Publishing Corp., New
York (1944)

16

29

1

50V6

CHROMIC ACID, CrO_3			Refs.
(Chromic Trioxide, Chromic Anhydride, Chromium (VI) Oxide, Red Oxide of Chromium)			Addnl. Ref. 8
Percent Oxygen :	48.00		
Specification No. :	(for technical grade) O-C-3038		
Molecular Weight :	100.01		
Crystalline Form :	rhombic	1A	
Color : red (color darkens with rise in temperature and is restored on cooling)		1A, 54V2	
Density, g./ml. :	(solid) 2.70	1A	
Coefficient of Thermal Expansion :	—		
Heat of Formation, Kcal./mole at 298°K :	-142.1 ± 1 -138.5 ± 2.5	Addnl. Ref. 7 24A	
Addnl. Ref. 8 gives literature values from -140 to -147			
Free Energy of Formation at 298°K :	-120.2	6	
BEAT AND FREE ENERGY OF FORMATION, $\text{CrO}_3(\text{c})$			2
T, °K	A H (cal./mole)	A F° (cal./mole)	
298.16	-140,000 (± 3000)	-121,000 (± 3500)	
400	-139,000	-114,500	
471	-139,000	-110,000	
471	-135,000	-110,000	
500	-134,500	-108,500	
600	-133,000	-103,500	
Entropy, cal./deg./mole at 298°K :	(solid) 17.5 17.2 ± 2.5	6 24A	
Free Energy Equations:			
<i>Reaction</i>		<i>Range of Validity, °K</i>	
1) $\text{Cr}(\text{c}) + \frac{3}{2} \text{O}_2(\text{g}) = \text{CrO}_3(\text{c})$		298.16 to 471	2
$\Delta F_T^\circ = -141,590 - 13.82T \log T + 103.90T$			
2) $\text{Cr}(\text{c}) + \frac{3}{2} \text{O}_2(\text{g}) = \text{CrO}_3(\text{l})$		471 to 600	
$\Delta F_T^\circ = -141,580 - 32.24T \log T + 153.14T$			
Melting Point, °C :	196 (with decomposition) 197	1A, 31 Addnl. Ref. 8	
Heat of Fusion, Kcal./mole	3.77	2	
Boiling Point, °K :	decomposes	1A	
Heat of Vaporization :	—		
Transition Point :	—		
Heat of Sublimation :	—		
Heat Content or Enthalpy:	—		
Heat Capacity :	—		

Chromic Acid, CrO₃ (page 2)

Decomposition Temperature :	above 230°C					29
For TCA see Addnl. Ref. 9						
For DTA and TGA see Refs. 33 and 54V2						
Decomposition Products	$\text{Cr}_3\text{O}_8, \text{Cr}_2\text{O}_8, \text{CrO}_2,$ $\text{Cr}_2\text{O}_3 + \text{O}_2$					54V2 Addnl. Refs. 4, 6
Vapor Pressure :	—					
X-Ray Crystallographic Data :						
System	Space Group	a	b	c	Molecules/ Unit Cell	Addnl. Ref. 5
orthorhombic	D _{2h} ¹⁶	5.70 ± 0.05	8.46 ± 0.03	4.77 ± 0.03	4	96
Hygroscopicity :	deliquesces above 35% R.H.					Addnl. Ref. 3
Solubility Data :						
In water :	166g./100 ml. at 15°C and 206.7 at 100°C					1A
In ether, alcohol, H ₂ SO ₄ :	soluble					
Health Hazard : Extremely toxic. Local irritant and systemic poison. L.D. (subcutaneously in dogs) 330 mg./kg. Concentrated solutions may cause dermatitis and local ulceration. Inhalation causes irritation to nasal mucosa and respiratory tract. Ingestion may cause nausea, vomiting, diarrhea, renal damage, and death. Caution — not for internal use.						29, 12
Safety Classifications :						
OSM :	not specifically mentioned					
ICC :	oxidizing material, yellow label					
M.C.A. :	warning label required					
Fire and Explosion Hazard : Dangerous ; may oxidize organic compounds with explosive violence. Contact with combustible material may cause fire and evolution of highly toxic fumes. Foamite is ineffective against a chromic acid fire as the acid supplies its own oxygen. Carbon tetrachloride should not be used on a chromic acid fire. Water is the only effective agent.						12, 29
Use in Pyrotechnics :	as an oxidizer					Addnl. Ref. 3
Additional References :						
1) "Preparation of Ferromagnetic Chromium Dioxide," B. Kubota, J. Phys. Soc. Japan 15,1706 (1960) (See note below)						
2) "Decomposition of Higher Oxides of Chromium under Various Pressures of Oxygen," B. Kubota, J. Am. Ceram. Soc. 44,239 (1961)						

Chromic Acid, CrO₃ (page 3)

Note : Both references above discuss the thermal decomposition of CrO₃ under high oxygen pressure resulting ~~from~~ the oxygen liberated from CrO₃ itself.

- 3) "Chromic Acid in the Metal Finishing Industry," Diamond Alkali Co., Cleveland, Ohio (1953)
- 4) "The Products of Thermal Decomposition of Chromium Trioxide," R. S. Schwartz et al., J. Am. Chem. Soc. **74,1676 (1952)**
- 5) "The Crystal Structure of Chromium Trioxide," A. Bystrom and K. A. Wilhelmi, Acta. Chem. Scand. **4, 1131 (1950)**. C.A. **45,3679 (1951)**
- 6) C.A. **45,21319 (1959)**
- 7) "The ~~Heat~~ of Formation of Ammonium Dichromate," C. A. Neugebauer and J. L. Margrave, J. Phys. Chem. **61, 1429 (1957)**
- 8) "Chromium," M. Judy, Reinhold Publishing Corp., New York (1956)
- 9) C.A. **42,422 (1948)**

CHROMIC OXIDE, Cr_2O_3
(Chromium (III) Oxide, Chromium Sesquioxide, Chrome Green, Green Cinnabar, Green Oxide of Chromium, Anadonis Green, Ultramarine Green, Chrome Ocher, Oil Green, Leaf Green, Green Rouge)

Percent Oxygen : 31.57
 Specification No. : not listed
 Molecular Weight : 152.02
 Crystalline Form : hexagonal
 Color: green

Commercial materials vary from a brownish green, to greyish green, to olive green to bright grass green.

Density g./ml. : (solid) 5.21

Coefficient of Thermal Expansion :

T, °C	% Linear Expansion bet. 100°C and Indicated Temp.	10 ⁶ X Mean Thermal Coeff. of Expansion bet. 100°C and Indicated Temp.
200	0.07	6.8
400	0.14	7.1
600	0.36	7.1
800	0.51	7.3
1000	0.66	7.3
1200	0.82	7.4

Heat of Formation, Kcal./mole at 298°K :
 -269.7
 -272.7 ± 4
 -272.65
 -268.5

a. HEAT AND FREE ENERGY OF FORMATION OF Cr_2O_3 (α , β)

T, °K	ΔH (cal./mole)	ΔF° (cal./mole)
298.16	-272,650 (± 350)	-253,150 (± 500)
298.16	-272,550	-253,150
400	-272,250	-246,550
500	-271,850	-240,200
600	-231,500	-233,900
700	-271,200	-227,650
800	-270,850	-221,450
900	-270,650	-215,250
1000	-270,450	-209,150
1100	-270,300	-203,000
1200	-270,150	-196,900
1300	-270,100	-190,800
1400	-270,100	-184,700

Refs.
 Addnl. Ref. 6

PA
 1A
 54V2
 1A

Addnl. Ref. 5

9, 31A
 Addnl. Ref. 4
 2
 Addnl. Ref. 3

Chromic Oxide, Cr₂O₃ (page 2)

T, °K	A H (cal./mole)	A F° (cal./mole)
1500	-270,150	-178,600
1600	-270,200	-172,450
1700	-270,300	-166,400
1800	-270,500	-160,250
1823	-270,550	-158,850
1823	-278,950	-158,850
1900	-279,000	-153,800
2000	-279,100	-147,200

Free Energy of Formation, Kcal./mole at 298°K : -250.3 ± 0.6

Entropy, cal./deg./mole at 298°K : 19.4

Addnl. Ref. 4

1A, 9, 31A

b. HEAT CONTENT AND ENTROPY Cr₂O₃ (c)

(Base α -crystals at 298.15°K)

4

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
298.16 (β) . .	100	0.34	1200	26,430	40.11
400	2740	7.94	1300	29,550	42.60
500	6540	14.19	1400	32,670	44.91
600	8380	19.36	1500	36,790	47.07
700	11,280	23.82	1600	38,920	49.08
800	14,230	27.76	1700	42,050	50.98
900	17,210	31.27	1800	45,180	52.77
1000	20,240	34.46	1900	48,320	54.47
1100	23,320	37.40	2000	51,460	56.08

Cr₂O₃ (β) :

$$H_T - H_{298.15} = 28.53T + 1.10 \times 10^{-5}T^2 + 3.74 \times 10^{-8}T^{-1} - 9758$$

(0.2 percent; 298° - 1800°K)

$$C_p = 28.53 + 2.20 \times 10^{-5}T - 3.74 \times 10^{-8}T^{-2}$$

Free Energy Equations :

Reaction	Range of Validity, °K
1) 2 Cr (c) + $\frac{3}{2}$ O ₂ (g) = Cr ₂ O ₃ (β)	298.16 to 1823
A F _T ^o = -274,670 - 14.07T log T + 2.01 × 10 ⁻⁵ T ² + 0.69 × 10 ⁻⁸ T ⁻¹ + 105.61T	
2) 2 Cr (l) + $\frac{3}{2}$ O ₂ (g) = Cr ₂ O ₃ (β)	1823 to 2000
A F _T ^o = -278,030 + 2.33T log T - 0.35 × 10 ⁻⁵ T ² + 1.57 × 10 ⁻⁸ T ⁻¹ + 58.29T	

Melting Point, °C : The range of values listed in the literature vary as much as 500°C.

Lowest value

1900

Highest value

2435

2

31A

Addnl. Ref. 5

Chromic Oxide, Cr₂O₃ (page 3)

Heat of Fusion, Kcal./mole :	25	,
Boiling Point, °K :	decomposes at 3300 ± 300	,
Transition Point, °K : C _{II} to C _I	306	, 41
	298	,
Heat of Transition, Kcal./mole :	0.1	,
Heat of Sublimation :	—	
Heat Content or Enthalpy :		
See Table b		
Heat Capacity :		
See Table b		
Decomposition Temperature :	3300 ± 300	3
See also Addnl. Ref. 1		
For DTA see 54V11		
Decomposition Products :	—	
Dissociation Pressure :		

Oxygen Pressures over Cr₂O₃

Addnl. Ref. 5

Press. atm.	7.4×10^{-25}	5.1×10^{-23}	3.8×10^{-22}
Temp. °C	895	968	1002

For Dissociation Pressure curve see Ref. 54V11

X-Ray-Crystallographic Data :

System	Space Group	a	c	Molecules/Unit Cell	
Hexagonal	D _{3d} ⁶	4.954	13.548 at 26°C	6	97V5

Hygroscopicity :

Solubility Data: In water:

insoluble

In acids, alkalies, or alcohol:

slightly soluble

Health Hazard : Poisonous. Corrosive on skin and mucous membranes.

Safety Classifications :

OSM :

not listed

ICC :

not listed

Fire and Explosion Hazard :

Electrostatic Sensitivity :

Use in Pyrotechnics : Product of the burning of chromium and some chromium compounds.

Additional References :

- 1) "Decomposition of Higher Oxides of Chromium under Various Pressures of Oxygen," B. Kubota, J. Amer. Ceram. Soc. **44,239 (1961)**
- 2) "The Volatilization of Chromium Oxide," D. Caplan and M. Cohen, J. Electrochem. Soc. **108,438 (1961)**

Chromic Oxide, Cr_2O_3 (page 4)

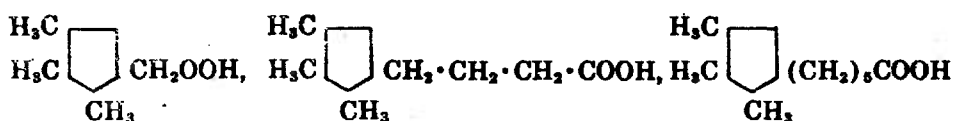
- 3) "Thermodynamics of the Oxidation of Chromium," J. N. Ramsey et al., *J. Electrochem. Soc.* *103*, 135 (1956)
- 4) "Heats of formation of chromium oxide and cadmium oxide from combustion calorimetry," A. D. Mah, *J. Am. Chem. Soc.* *76*, 3363 (1954)
- 5) "Chromium," M. Judy, Reinhold Publishing Corp., New York (1956)

COBALT NAPHTHENATE

Cobalt naphthenate is a solution of the cobalt salts of mixed naphthenic acids in mineral spirits. The product contains about **6%** cobalt and is **stand-**
ardized on this basis. Chemical and physical properties of cobalt naphthenate cannot be described in the usual manner because the naphthenic acid usually represents a mixture of various cyclopentane monocarboxylic acids, containing on the average about **12** carbon atoms. The carboxyl group is usually separated from the cyclopentane group by at **least** one methylene group, but sometimes **there may be more** than one. **The balance of the carbons is made up by** alkyl substitution on the cyclopentane nucleus. The acids vary considerably depending on the particular source of the petroleum crude from which they are derived. The cobalt is primarily in the cobaltous form.

Chemically the naphthenic acids have been classified as carboxylic acids of the general formulas $C_nH_{2n-2}COOH$ and $C_nH_{2n-4}COOH$, with **most** of them in the first group. They are derivatives of the 2,3,4-trimethylcyclopentane alkane acids, e.g.

Structural Formula :



Commercially available naphthenic acids are identified by origin and acid number. The lack of a more definite classification is due to the complexity of the mixed acids now known as naphthenic acids and to the absence of information correlating the properties of the acids from different sources.

The general formula has been given as approximately $Co(RCOO)_2$, where R is largely a mixture of trimethylcyclopentane alkane radicles.

Specification No. :

TT-D-643

Specification Requirements :

Metal (cobalt), % :	(min.) 5.7 (max.) 6.3
Non-volatile, % :	(max.) 70
sp. Gr. :	(min.) 0.950 (max.) 1.050
Flash Pt. (closed cup), °F :	(min.) 100

The volatile matter shall be mineral spirits.

Color:	red-blue to purple	50V5
Density, g./ml. :	0.947 to 0.965	50V5
Melting Point :	398°K (125°C)	50V5
Solubility :	soluble in benzene	50V5
Health Hazard : In the stomach, cobalt naphthenate hydrolyzes to $CoCl_2$. Although this compound has been used medicinally in cases of iron deficiency (anemia), in doses larger than 100mg. $CoCl_2$ is toxic.		29V5

. Refs.

Addnl. Ref. 1

Addnl. Ref. 2

Addnl. Refs.
2, 3

50V5

Cobalt Naphthenate (page 2)

Safety Classification:

OSM : not listed

ICC : not listed

Fire and Explosion Hazard: _____

Electrostatic Sensitivity: _____

Nuodex Products Co. specifications for Cobalt Naphthenate (DMRCobalt 6%) : Addnl. Ref. 1

Metal content, % : 6.0 ± 0.1

Color (Gardner); max. : violet blue

Sp. Gr.: 0.935 - 0.980

lbs./gal. (at 80°F) : 7.75 - 8.15

Solids, % max. : 67

80°F Viscosity (max.), Cardner : A, 0.50 poises

20°F Viscosity (max.), Gardner : K, 2.75 poises

Flash Pt. (Pensky-Marten closed cup), °F: 104

Use in Pyrotechnics: As a paint drier. As a catalyst with Laminac 4116 and Lupersol DDM (q.v.).

Additional References:

- 1) Private communication from W. J. Stewart, Nuodex Products Co., Elizabeth, N. J.
- 2) "Naphthenic Acids and Derivatives," E. R. Littmann and J. R. Klotz, Chem. Revs. 30, 97 (1942)
- 3) "A Manual of Organic Chemistry," G. M. Dyson, Longmans, Green and Co., New York (1950)

COPPER, Cu				Refs.
Specification No. :	JAN-C-768			
Molecular Weight :	63.54			
Crystalline Form :	cubic			1
Color :	reddish metal			1
Density, g./ml. :	(solid) 8.93-8.95			1
Coefficient of Thermal Expansion :				
	Temp. Range, °C	Coefficient		1
linear	-191 to + 16	14.09×10^{-6}		
(electrolytic) linear	25 to 100	15.8×10^{-6}		
	25 to 300	17.8×10^{-6}		
	0 to 600	16.07×10^{-6}		
Equation for Linear Expansion: $l_t = l_0 (1 + .1596t + 0.102t^2)$				1
where l_t and l_0 are the lengths at the temperature $t^\circ\text{C}$ and 0°C				
Heat of Formation, Kcal./mole at 298°K :	(gas) 81.1			5
Free Energy of Formation, Kcal./mole at 298°K :	(gas) 71.628			5
Entropy, cal./deg./mole at 298°K :	7.97			5
See Tables a, b, and c				
Melting Point :	1356°K (1083°C)			5
Heat of Fusion, cal./mole :	3120			4, 5
Boiling Point :	2855°K (2582°C)			5
Heat of Vaporization, cal./mole :	72,800			5
Transition Point:	—			
Heat of Sublimation, cal./mole at 298°K :	81,000			5
Heat Content or Enthalpy, cal./mole at 298°K :	(solid) 1201			5
	(gas) 2116			9
See Tables a, b, and c				
a. HEAT CONTENT AND ENTROPY OF Cu(c, 1)				4
(Base, crystals at 298.15°K; atomic wt. 63.54)				

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	600	1.73	1100	5190	8.28
500	1215	3.10	1200	5895	8.90
600	1845	4.25	1300	6615	9.47
700	2480	5.23	1357 (c) . . .	7040	9.79
800	3130	6.10	1357 (l) . . .	10,160	12.09
900	3800	6.80	1400	10,480	12.32
1000	4490	7.61	1500	11,230	12.84

(page

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg.	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15}
1600	11,980	13.33	2200	16,480	15.71
1700	12,730	13.78	2400	17,980	16.37
1800	13,480	14.21	2600	19,480	16.97
1900	14,230	14.62	2800	20,980	17.52
2000	14,980	15.00			

Cu(c) :

Enthalpy : $H_T - H_{298.15} = 5.41T + 0.75 \times 10^{-5}T^2 - 1680$ (0.3 percent ; 298° - 1357°K)

Heat Capacity : $C_p = 5.41 + 1.50 \times 10^{-5}T$

Cu(l) :

Enthalpy : $H_T - H_{298.15} = 7.50T - 20$ (0.1 percent ; 298° - 2800°K)

Heat Capacity : $C_p = 7.50$

b. XEAT CONTENT AND ENTROPY OF Cu(g)

(Base, ideal gas at 298.15°K; atomic wt., 63.54)

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	505	1.46	1900	7985	9.22
500	1005	2.57	2000	8495	9.48
600	1500	3.48	2200	9530	9.97
700	1995	4.24	2400	10,590	10.43
800	2495	4.90	2600	11,680	10.87
900	2990	5.49	2800	12,815	11.29
1000	3490	6.01	3000	13,995	11.70
1100	3985	6.49	3500	17,155	12.67
1200	4480	6.92	4000	20,600	13.59
1300	4980	7.32	4500	24,290	14.46
1400	5475	7.69	5000	28,150	15.27
1500	5975	8.03	6000	36,160	16.73
1600	6475	8.35	7000	44,450	18.01
1700	6975	8.66	8000	53,175	19.17
1800	7480	8.94			

Cu(g) :

Enthalpy : $H_T - H_{298.15} = 4.97T - 1482$ (0.1 percent ; 298° - 2000°K)

Heat Capacity : $C_p = 4.97$

Enthalpy : $H_T - H_{298.15} = 2.861T + 0.53 \times 10^{-5}T^2 + 655$ (0.2 percent ; 2000° - 5000°K)

Heat Capacity : $C_p = 2.86 + 1.06 \times 10^{-5}T$

Copper, Cu (page 3)

c. HEAT CAPACITY OF COPPER

Solid from 298 to 1356°K	
Liquid from 1356 to 2855°K	
Gas from 2855 to 3000°K	
t, °K	C _p ° (cal./deg./mole)
298	5.85
400	6.01
600	6.31
800	6.61
1000	6.91
1300	7.36
1400 to 2800	7.50
2900	5.89
3000	6.01

Decomposition Temperature : ———

Decomposition Products : ———

Vapor Pressure :

Press. " Hg.	1	10	40	100	400	760	B.P.
Temp. °C	1628	1879	2067	2207	2465	2595	1083

X-Ray Crystallographic Data :

System	Space Group	a	Atoms/Unit Cell
cubic	O _h ⁸	3.608	4

Hygroscopicity : (Reduced Cu) cumulative increase in weight after

storage over water for 29 days: 1.9%

storage over H₂SO₄ for 29 days: 1.0%

2 days in oven at 105°C: 0.9%

In moist air gradually forms green basic copper carbonate, CuCO₃·Cu (OH)₂

Solubility Data: In water: insoluble

In HNO₃, hot H₂SO₄ : soluble

In HCl, NH₄OH, acetic acid : very slightly soluble

Health Hazard : Copper is not considered an industrial poison. It is moderately toxic when inhaled or ingested.

Safety Classification :

OSM: class 2

Fire and Explosion Hazard : The powdered metal is a dangerous fire hazard when exposed to flame or hot sparks. By chemical reaction with oxidizers it may explode. It burns with intense heat. Precautions should be taken to prevent water from contacting the material. Store and process only in buildings adequately vented to prevent accumulation of evolved hydrogen

Copper, Cu (page 4)

which results from the reactions of powdered metal and moisture. in the repair or maintenance of buildings use only non-sparking tools after the metal powder or dust has been removed. In fighting fire use no water; use powdered graphite, dolomite, or sodium chloride.

Electrostatic Sensitivity :	not ignited by electric spark	49

Ignition Temperature: (Reduced Cu)

Dust Cloud, °C :	700	49

Quiescent Powder :	oxidized rapidly at 270°C with no ignition	51

Use in Pyrotechnics: Copper is used as a fuel. It produces a blue-green color in burning compositions.	20, 50

Additional Reference :

- 1) Ref. 64

CUPROUS OXIDE, Cu₂O
(Cuprite)

Refs.

Specification No.:	MIL-C-15169	
The spec. covers two types, Type I and Type II, which differ in purity.		
Molecular Weight:	143.08	
Crystalline Form:	octagonal, cubic	1
Color:	yellow, orange, red, or dark brown, according to the method of preparation	79
Density, g./ml.:	(solid) 6.0	1
Coefficient of Thermal Expansion, cubic at 40°C:	2.79×10^{-6}	54V3
	linear at 40°C: 9.3×10^{-7}	
Heat of Formation, Kcal./mole at 298°K:	39.84	1, 9
See Table a		
Free Energy of Formation, cal./mole at 298°K:	-34.98	1, 9
See Table a		

a. HEAT AND FREE ENERGY OF FORMATION OF Cu₂O (c, 1)

T, °K	H (cal./mole)	F° (cal./mole)
298.16. . . .	-40,400 (± 1550)	-35,000 (± 1500)
400	40,200	-33,200
500	-40,100	-31,500
600	-39,900	-29,800
700	-39,700	-28,200
800	-39,500	-26,500
900	-39,300	-24,900
1000	-39,000	-23,300
1100	-38,800	-21,800
1200	-38,400	-20,200
1300	-38,000	-18,700
1357	37,700	-17,900
1357	-43,900	-17,900
1400	-43,700	-17,100
1500	43,100	-15,200
1502	-43,100	-15,200
1502	-29,700	-15,200
1600	-29,200	-14,200
1700	-28,800	-13,300
1800	-28,300	-12,400
1900	-27,800	-11,600
2000	-27,480	-10,700

Phase Changes of Metal
M.P., 1357°K
ΔH = 3120 cal./g.-atom

Cuprous Oxide, Cu₂O (page 2)

Entropy, cal./deg./mole at 298°K:	24.1 22.44	3, 4, 9 2
Melting Point:	1502°K (1229°C)	2, 9
Heat of Fusion, Kcal./mole	13.4	2, 7, 9
Boiling Point:	loses oxygen at 2073°K (1800°C)	1
Transition Point:	—	
Heat of Sublimation:	—	

**b. HEAT CONTENT AND ENTROPY OF Cu₂O(c)
(Base, crystals at 298.15°K)**

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	1720	4.96	900	11,000	19.98
500	3470	8.87	1000	13,020	22.10
600	5280	12.26	1100	15,120	24.10
700	7150	15.14	1200	17,320	26.02
800	3050	17.68			

Cu₂O(c) :

Enthalpy : $H_T - H_{298.15} = 14.90T + 2.85 \times 10^{-5}T^2 - 4696$
(0.2 percent ; 298° - 1200°K)

Heat Capacity : $C_p = 14.90 + 5.70 \times 10^{-5}T$

Heat Capacity, cal./deg./mole at 298°K : (solid) 16.7

Decomposition Temperature: When heated in air **starts** to oxidize slowly at **about 145°C**, and rapidly towards 285°C.

Heated in air it does not dissociate but oxidizes.

Decomposition Products :

Ref. 54V3 states that at high temperature Cu₂O dissociates into copper and oxygen.

Dissociation Pressure :

Press. mm.	.02865	.0316	.0328	.038	.138	.446	8.312	40.19
Temp. °C	500	1000	1500	1800	1900	2000	2300	2500

X-Ray Crystallographic Data :

System	Space Group	a	Molecules/Unit Cell
cubic	O _h ¹	4.26	2

Hygroscopicity: Cuprous oxide is stable in dry air, but gradually oxidizes to cupric oxide, CuO, in moist air.

46

44V60B

54V3,
Addnl. Ref. 1

1

29

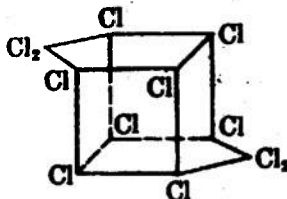
Cuprous Oxide, Cu₂O (page 3)

Solubility Data: In water and alcohol:	insoluble	1
In HCl, NH ₄ Cl, NH ₄ OH :	soluble	
In HNO ₃ :	slightly soluble	
Health Hazard:	slight	12
Safety classifications:		
OSM :	not listed	
ICC :	not listed	
Fire and Explosion Hazard:	—	
Electrostatic Sensitivity :	—	
Use in Pyrotechnics: Cuprous oxide is used as a fuel, and with chlorinated organic compounds as a color intensifier.		17
Additional References :		
1) E. Heyn, Zeit. anorg. Chem. 39, 1 (1904)		

"DECHLORANE," $C_{10}Cl_{12}$
(Dimer of Hexachlorocyclopentadiene)

Note: The name "Dechlorane" is trademarked by the Hooker Chemical Corp.

Formula :



Refs.

Addnl. Ref. 3

Addnl. Refs.
1, 2, 4

Specification No. :	not listed	
Molecular Weight :	545.6	
% Chlorine:	78.8	
Crystalline Form:	granular solid	
Color :	white	Addnl. Ref. 1
Density :	2.020 $\pm$ 0.005 g./cc. at 24.3°C	Addnl. Ref. 1
coefficient of Thermal Expansion :	—	
~~Heat~~ of Formation:	—	
Free Energy of Formation:	—	
Entropy :	—	
Melting Point, °C:	(sealed tube method) 485	Addnl. Refs. 1, 2, 33
In a DTA run liquifaction started at about 160°C		
Heat of Fusion:	—	
Boiling Point, °C:	starts to sublime about 240	Addnl. Ref. 1
Transition Point :	—	
~~Heat~~ of Sublimation :	—	
Heat Content or Enthalpy:	—	
Heat Capacity :	—	
Decomposition Temperature :		33
White fumes noted bet. 300°-500°C. These fumes darkened as the temp. was raised. Some decomposition above 500°C.		
For DTA see Ref. 33		
Decomposition Products :	—	

Decchlorane, C₁₀Cl₁₂ (page 2)

Vapor Pressure :

Press. mm.	3×10^{-7}	6×10^{-6}	3×10^{-1}	Addnl. Ref. 1
Temp. °C	25	50	197	

X-Ray Crystallographic Data : ———

Hygroscopicity : ———

solubility Data: In benzene:

soluble

Addnl. Ref. 3

Solvent**g./100 g. solvent at R.T.**

Addnl. Ref. 1

toluene

16.3

xylene

32.7

perchloroethylene

10.3

styrene

17.2

mineral spirits (Stoddard solvent)

5.8

Reactivity: Decchlorane is inert to strong oxidizing and reducing agents such as H₂SO₄, HNO₃, aq. NaOH, LiAl, H₂, ClSO₃H, H₂ and O₂ under normal reaction conditions. Unaffected by Zn dust plus HCl, acetic acid or methanol, also by oxidizing agents such as KMnO₄, CrO₃ and SO₃.

Addnl. Ref. 1

Addnl. Ref. 2

Health Hazard : Only slightly toxic. Essentially not irritating to the skin. Oral

Addnl. Ref. 1

E.D. 50 (value determined on rats) approx. 6000 mg./kg.

Safety Classifications:**OSM :**

not listed

ICC :

not listed

Fire and Explosion Hazard: ———

Electrostatic Sensitivity : ———

Use in Pyrotechnics:

as a color intensifier

Additional References :

- 1) Data obtained from literature prepared by the Hooker Chemical Corp., Niagara Falls, N. Y.
- 2) "An Investigation of the Chlorocarbon, C₁₀Cl₁₂, M.P. 485° and the Ketone, C₁₀Cl₁₀O, M.P. 349°," E. T. McBee et al., J. Am. Chem. Soc. **78**, 1511 (1956)
- 3) "The Chemical Behavior of Hexachlorocyclopentadiene. II. Condensation with Trichloroethylene," J. S. Newcomer and E. T. McBee, J. Am. Chem. Soc. **71**, 952 (1949)
- 4) "The Structure of the Compound C₁₀Cl₁₂," D. H. Zijp and H. Gerding, Rec. trav. chim. **77**, 682 (1958)

DEXTRIN

(Starch Gum, British Gum, Amylin, Gommelin, Vegetable Gum)

Dextrin or dextrines are obtained by treating starch in any one of a number of ways. These include controlled dilute acid hydrolysis of wet starch, the use of certain enzymes, and dry heat. The resultant products, whose properties vary with the source of the starch and the details of the treatment, are represented by the general chemical formula $(C_6H_{10}O_5)_n \cdot H_2O$. The n is, however, much smaller than in the original starch. The various dextrinization treatments of starch lead to complex mixtures resulting from three main types of reaction :

- 1) Hydrolytic cleavage, which yields smaller and more water soluble compounds.
- 2) Transglucosidation, in which a 1-4 glucosidic bond between two $C_6H_{10}O_5$ units is broken and a 1-6 bond formed with a different $C_6H_{10}O_5$ unit, with the formation of a branch point. This reaction produces branched molecules and little change in molecular weight.
- 3) Some repolymerization and condensation of smaller molecules.

Because the polymolecularity of the original starches differ and various treatments result in a mixture of the three main reactions, the products differ in size, distribution of molecules, and in extent of branching, and thus have different properties.

Dextrins are distinguished from starch by the violet and red colors that dextrins give with iodine solution.

Dextrins are usually characterized by giving the source or kind of starch used, the color of the dry products, their solubility in water, and the viscosity of their water dispersions. The following table gives the more common treatments of starch to produce dextrins, together with some properties of the resulting starches.

CLASSIFICATION OF DEXTRINS

	<i>White Dextrins</i>	<i>Yellow or Canary Dextrins</i>	<i>British Gums</i>
<i>Manuf. Conditions</i>			
Usual catalyst	HCl	HCl	none or an alkali
Temperature, °C	79-121	149-218	135-218
Time, hrs.	3-8	6-18	10-20
<i>Product Characteristics</i>			
Color	white to light cream	buff to yellow or brown	buff to dark brown
Solubility (dispersibility), %	1-98	90-100	1-100
Useful diln., parts of water	2-5	1 or less	3-10

Refs.

1, 16, 23, 24,
29, 70

23

Dextrin (page 2)

Specification:

JAN-D-232

The specification covers **two** types of **corn** dextrin: *Type I*—white, and *Type II*—yellow. These vary in composition **as** indicated by a wide difference in water solubility.

Molecular Weight:

variable (appreciably
less than starch)

Color:

white to dark brown

Density, g./ml.:

1.0384

1

Melting Point:

decomposes

Specific Heat, cal./g./°C at 90°C:

0.292

1

Hygroscopicity:

very deliquescent

20V3

Health Hazard:

non toxic

93.

Safety Classifications:

OSM:

not listed

ICC:

no shipping label required

Use in Pyrotechnics:

fuel and binder

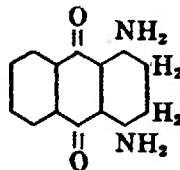
Dextrins have strong adhesive properties and **are** used mainly **as** pastes.

Additional References:

- 1) B. Brimhall, Phd. Eng. Chem. *36*, 72 (1944)
- 2) J. Geerdes et al., *J. Am. Chem. Soc.* **79,4209 (1957)**
- 3) "Chemistry and Industry of Starch," R. W. Kerr, Ed., Academic Press, Inc., New York (1950)
- 4) G. M. Christensen and F. Smith, *J. Am. Chem. Soc.* **79,4492 (1957)**

1,4-DIAMINO-2,3-DIHYDROANTHRAQUINONE
(1,4-diamino-2,3-dihydro-9,10-dihydro-9,10-diketoanthracene,
Violet A 100)

Structural Formula :



Specification No. :

MIL-D-3668

Covers one grade with a minimum purity of 87%.

Molecular Weight :

240.26

Color :

violet

Density, g./ml. :

(apparent) 0.35 ± 0.10

Solubility :

soluble in 95% alcohol

Health Hazard : Some toxicity as indicated by the specification requirement that each container be conspicuously labelled : "CAUTION—Avoid skin contact or breathing of dust fumes. Provide adequate ventilation in work areas."

Safety Classifications:

OSM:

not listed

ICC:

not listed

Use in Pyrotechnics: To impart a violet color to burning smoke mixtures.

Refs.

82

Spec.

Spec.

DIATOMACEOUS EARTH

(Infusorial earth, "**Diatomite**," fossil flour, **Kieselguhr**, **Triplite**,
Siliceous earth, **Tripoli** (a type of crystalline diatomite),
"**Celite**," "**Featherstone**," "**Filter-Cel**," **Super-Mom**)

Diatomaceous earth is composed of the siliceous skeletons of diatoms, which are microscopic aquatic plants of the class Bacillieriae. These occur in great beds and are not earthy. Large deposits occur in the western part of the U.S. after being dug from open pits, the diatomite is prepared for commercial use usually by being heated to remove organic matter and treated with acids to remove iron. The individual diatoms occur in a great many forms and differ considerably in size. The average particle size varies from 1 to 40 μ and the specific surface from about 7.050 to as much as 67,000 sq. cm./g. Chemically, diatomite is mainly silica (usually the SiO₂ content is between 84 and 92%).

The impurities are highly variable and are usually Al and Fe oxides. The water content varies from 2 to 10%. The physical properties also vary over a wide range.

Diatomaceous earth is frequently used because of its highly absorptive character which is closely related to its specific surface. Oil absorption varies from 25 to 150 lbs. of oil per 100 lbs. of diatomite; water from one to four times the weight of diatomite. This porosity is a result of the fact that the shells of the diatoms are hollow.

Diatomite is a poor conductor of heat, electricity, and sound, and makes an excellent filter.

Specification :

MILD-20550

The specification requires that the material be a naturally mined diatomaceous earth which has not been ignited.

SiO₂ content, % : 85.0 to 87.0

Organic matter, % : max. 1.0

Linseed absorption, g. oil/100 g. material : 150 to 210

Normal color and form: white to light gray, to pale buff fine powder, varies with the nature of the impurities present

Density g./ml. :

noncalcined 1.90

calcined and bleached, whitest grades 2.35

Apparent : 0.24 to 0.34

Spec. requirement: (max.) 0.3

Melting Point: Uncontaminated diatomaceous earth should melt at the temp of fusion of silica, i.e., 1873°K (1600°C). The average quality sinters a about 1073°K (800°C).

Specific Heat: cal./g./deg. at 25°C : 0.23

Hygroscopicity : —

Refs.

50V10, 16,
Addnl. Ref. 1

52V3, 29

Addnl. Ref. 2

50V10

Addnl. Ref. 2

Addnl. Ref. 2

Diatomaceous Earth (page 2)

Solubility Data: Insoluble in water, acids, and dilute alkalis. Resistant to most chemicals. Attacked by HF and slowly dissolved by hot aqueous caustic alkali. **29, 52**

Health Hazard: Moderately toxic on inhalation. Under long exposure to high concentrations the dust may cause pulmonary fibrosis. **93, 29**

Fire and Explosion Hazard: none mentioned

Use in Pyrotechnics: as an inert filler

Additional References :

- 1) "Clarifying Efficiency of Diatomaceous Filter Aids," A. B. Cummins, Ind. Chem., **34**, 403 (1942)
- 2) "Diatomaceous Earth," R. Calvert, ACS Monograph No. 52, Chemical Catalogue Co., New York (1930)

DIBUTYLPHTHALATE

(n-butylphthalate, dibutyl-o-phthalate, butyl phthalate,
dibutyl-1,2-benzenedicarboxylate)

Ref.

Formula : $C_6H_4(COOC_4H_9)_2$ or $C_{18}H_{22}O_4$

The industrial product made by the Commercial Solvents Corp. has the following properties: Purity, 99-100% ; Boiling Range at 37 mm. press., 227-235°C; M.P. < -10°C; Flash Point, 347°F.

Specification No. :	JAN-D-218	
Molecular Weight :	278.34	
Form :	oily liquid	1
Color :	colorless	1
Density, g./ml. :	(liquid) 1.0465 1.0427	1 Addnl. Ref. 2
Coefficient of Thermal Expansion :	—	
Heat of Formation, Kcal./mole at 18°C:		Addnl. Ref. 1
At constant pressures :	-207.2	
At constant volume :	-199.6	
Free Energy of Formation :	—	
Entropy :	—	
Melting Point:	238°K (-35°C)	
Heat of Fusion:	—	
Boiling Point:	622°K (349°C) 613°K (340°C)	29 31A
Transition Point :	—	
Heat of Sublimation:	—	
Heat Content or Enthalpy :	—	
Heat Capacity:	—	
Decomposition Temperature :	—	
Decomposition Products :	—	
Vapor Pressure:		
— Press mm.	1	PO
	40	100
	400	760
Temp. °C	148.2	198.2
	235.8	263.7
	313.5	340
See also Addnl. Ref. 2		
X-Ray Crystallographic Data :	—	
Hygroscopicity:	—	
Solubility Data: In water:	0.04 g./100 ml. at 25°C	1
Miscible in all proportions with alcohol, ether, acetone, benzene, and many organic liquids.		

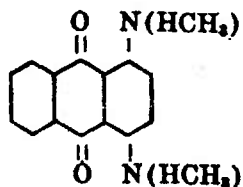
Health Hazard : Low ; ingestion <i>can cause</i> gastrointestinal disturbances.	29
Safety Classifications:	
OSM: Listed as substantially inert and presenting no particular fire or toxic hazard as used in Ordinance establishments.	
ICC :	not listed
Fire and Explosion Hazard: Combustible on exposure to heat or flame . Can react with oxidizing materials . To fight fire use water, foam, CO₂ , dry chemical, or CCl ₄ .	75
Heat of Combustion, Kcal./mole at 20°C (H ₂ O liquid) :	1536.2
Flash Point, °F (<i>closed</i> cup) :	315
(<i>open</i> cup) :	335
Autoignition Temperature, °F :	757
Use in Pyrotechnics: As a solvent for nitrocellulose.	67, 71
Additional References:	
1) L. Médard, <i>Mém. artillerie franc</i> , 28,476 (1954)	
2) "The Vapour Pressure of di-n-butylphthalatedi-n-butylsebacate, Lauric Acid and Myristic Acid," E. Hammer and A. L. Lyderson, <i>Chem. Eng. Sci.</i> 1, 66 (1957)	

1,4-DI(METHYLAMINO)ANTHRAQUINONE
(1,4-bis(methylamino)-anthraquinone; Duranol Brilliant Blue G,
Celliton(e) Fast Blue B; CI 61500, CI Disperse Blue 14)

Refs.

Structural Formula :

$C_{16}H_{14}N_2O_2$



Specification No. :	MILD-21354
Molecular Weight :	266.30
Crystalline Form :	—
Color:	blue
Density :	—
Coefficient of Thermal Expansion :	—
Heat of Formation:	—
Free Energy of Formation:	—
Entropy:	—
Melting Point:	494-6°K (221-3°C)
Spec. min.:	482°K (209°C)
Heat of Fusion:	—
Boiling Point:	—
Transition Point :	—
Heat of Sublimation :	—
Heat Content or Enthalpy:	—
Heat Capacity:	—
Decomposition Temperature:	—
For DTA and TGA see Ref. 80	
Decomposition Products :	—
Vapor Pressure :	—
X-Ray Crystallographic Data :	—
Absorption Spectra, see Ref. 66	
Hygroscopicity:	—
Solubility Data (mg./100 ml.),	
In water at 25°C:	< 0.00002
at 80°C:	0.0002

Addnl. Ref. 1

Addnl. Ref. 2

Addnl. Ref. 3

1,4-Di(methylamino)anthraquinone (page 2)

(g./l. at 25°C) in C₂H₅OH: 0.12

In ethyl acetate: 0.86

In benzene: 1.9

Health Hazard: toxicity unknown

The spec. requires that each container be conspicuously labeled, "Caution. Avoid skin contact or breathing of dust or fumes. Provide Adequate Ventilation."

Safety Classifications:

OSM: not listed

ICC: not listed

Fire and Explosion Hazard:

Electrostatic Sensitivity:

Use in Pyrotechnics:

to color smoke
mixtures blue

Additional References:

1) C.A. 47,870 (1953)

2) J. Soc. Dyers Colourists 70, 68-77 (1954)

92

4-DIMETHYLAMINOAZOBENZENE
(Benzeneazodimethylaniline ; N,N-dimethyl-p-phenylazoaniline;
Sudan Yellow GGA, butter yellow; methyl yellow,
C.I. 11020, C.I. Solvent Yellow 2)

Structural Formula :		$C_{14}H_{15}N_3$	
Specification No. :	XPA-PD-367 (Rev. 1)		
The spec. requires amin. purity of 98%.			
Molecular Weight :	225.30		
Crystalline Form :	leaflets		1, 29
Color :	yellow		1
Density :	—		
Coefficient of Thermal Expansion :	—		
Heat of Formation :	—		
Free Energy of Formation :	—		
Entropy :	—		
Melting Point :	388°K (115°C) 390°K (117°C)		48 Addnl. Ref. 1
Heat of Fusion:	—		
Boiling Point:	—		
Transition Point :	—		
Heat of Sublimation, Kcal./mole :	28.9		Addnl. Ref. 2
Heat Content or Enthalpy:	—		
Heat Capacity :	—		
Decomposition Temperature :	For TGA see Ref. 80		
Decomposition Products :	—		
Vapor Pressure m_{μ} Hg between 86° and 108° = $a + (b \times 10^3/T)$			
$a = 17.57 \pm 0.13, b = -6.31 \pm 0.05, T = \text{absolute temp.}$			
	Temp. °C	100 110 115	Addnl. Refs. 1, 2
	V.P. μ	7.52 12.4 20.2	Addnl. Ref. 2
Energy of Volatilization, Kcal./mole at 264–361°C (96% purity) :	21.2		
X-Ray Crystallographic Data :	—		80
Hygroscopicity :	—		
Solubility Data (g./100 g.)			
In water at 25°C:	0.00003		
at 80°C :	0.0008		
In pyridine:	about 28		
			88V16I

Refs.

1, 29, 48, 48A

1, 29

1

48

Addnl. Ref. 1

Addnl. Ref. 2

Addnl. Refs.
1, 2

Addnl. Ref. 2

80

Addnl. Ref. 3

88V16I

4-Dimethylaminoazobenzene (page 2)

In alcohol, benzene, chloroform, ether, petroleum ether, oils, and mineral acids.:	soluble	29
Health Hazard :	may cause cancer	29, 84
The spec. requires that "Each container shall be conspicuously labeled : "CAUTION—Avoid skin contact or breathing of dust or fumes. Provide adequate ventilation."		
Safety Classifications :		
OSM :	not listed	
ICC :	not listed .	
Fire and Explosion Hazard:	—	
Heat of Combustion, cal./mole. Cp :	1909.6	88V16
cv :	1908.3	
Electrostatic Sensitivity :	—	
Use in Pyrotechnics:	to color smoke mixtures yellow	
Additional References :		
1) "The Vapor Pressures and Heats of Sublimation of p-Nitroaniline, NN-Dimethyl-p-nitroaniline, p-aminoazobenzene and NN-Dimethyl-p-aminoazobenzene," T. G. Majury, Chem. & Ind. 1956,349		
2) "The Dyeing of Cellulose Acetate with Non-Ionic Dyes. III. Dyeing from the Vapour Phase," T. G. Majury, J. Soc. Dyers Colourists 72, 41 (1956)		
3) J. Soc. Dyers Colourists, 70, 68-77 (1954)		

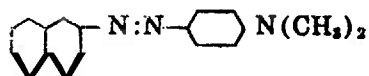
2-(4-DIMETHYLAMINOAZOPHENYL) NAPHTHALENE

Refs.

(4- β -naphthaleneazodimethylaniline;
 β -naphthaleneazo-4-dimethylaniline;
N,N-Dimethyl-p-2-Naphthylazo Aniline)

Structural Formula:

$C_{18}H_{17}N_3$



Specification No.:	MIL-D-3613
Molecular Weight:	275.36
Crystalline Form:	—
Color:	brownish-yellow
Density:	—
Coefficient of Thermal Expansion:	—
Heat of Formation:	—
Free Energy of Formation:	—
Entropy:	—
Melting Point:	445°K (172°C) 447°K (174°C)
Heat of Fusion:	—
Boiling Point:	—
Transition Point:	—
Heat of Sublimation:	—
Heat Content or Enthalpy:	—
Heat Capacity:	—
Decomposition Temperature:	—
Decomposition Products:	—
Vapor Pressure:	—
X-Ray Crystallographic Data:	—
For Absorption Spectra see Addnl. Refs. 3, 4, 5	
Hygroscopicity:	—
Solubility Data (g. to dissolve 1 g. dye):	
In toluene or CCl_4 :	70
In benzene:	soluble
Health Hazard:	—
Safety Classification:	
OSM:	not listed
ICC:	not listed

Addnl. Ref. 1
Addnl. Refs.
2, 5

Addnl. Refs.
2, 3

2-(4-dimethylaminoazophenyl) Naphthalene (page 2)

Fire and Explosion Hazard : ———

Electrostatic Sensitivity : ———

Use in Pyrotechnics : to color smoke mixtures
yellow

Additional References :

- 1) "Condensation of aromatic amines with nitranilines. Preparation of azoamine compounds," M. Martynoff, Compt. rend. 227, 1373 (1948)
- 2) "Zur Kenntniss der Diazoaminokörper," H. Goldschmidt and B. Bardach, Ber. 20, 386 (1928)
- 3) "Some Azo Dyes in Non-Aqueous Solvents," C. May and H. Hunt, Ind. Chem. 20, 386 (1928)
- 4) "Absorption spectra and structure of aminoazo derivatives," M. Martynoff, Compt. rend. 236, 88 (1953) ; "Physical Properties of the Aminoazobenzene Dyes. Absorption Spectra in Acid Solution," E. Sawicki, J. Org. Chem. 22, 1084 (1957)
- 5) "Physical Properties of the Aminoazobenzene Dyes. IX. Absorption Spectra in Alcohol and Acid Solution of Disazobenzene Dyes," E. Sawicki, J. Org. Chem. 23, 532 (1958)

DIPHENYLAMINE (<i>n</i> -phenylaniline, Anilinobenzene)								Refs.
Formula :	(C ₆ H ₅) ₂ NH							
Specification No. :	JAN-D-98							
Molecular Weight :	169.22							
Crystalline Form :	monoclinic							1
Color:	colorless leaflets (darkens on exposure to light)							1
Density, g./ml. :	(solid) 1.159							1
Coefficient of Thermal Expansion:-	—							
Heat of Formation, Kcal./mole at 18°C :								
at constant pressure :	-28.2							Addnl. Ref. 1
at constant volume:	-31.7							
Free Energy of Formation:	—							
Entropy :	—							
Melting Point:	326°K (53°C)							1
Heat of Fusion, cal. (15°C)/g.:	25.2							1
Boiling Point:	575°K (302°C)							1
Transition Point :	—							
Heat of Sublimation :	—							
Heat Content or Enthalpy:	—							
Heat Capacity:	—							
Decomposition Temperature:	—							
Decomposition Products :	—							
Vapor Pressure :								1
Press. mm.	1	10	40	100	400	760	M.P.	
Temp. °C	108.3	157.0	194.3	222.8	274.1	302.0	52.9	
X-Ray Crystallographic Data :								
System	a	b	c	Axial Angle		Molecules/Unit Cell		1
monoclinic	14.0	33.9	39.5	β = 91°30'		32		
Hygroscopicity :	—							
Solubility Data (g./100 ml.)								1
In water at 25°C :	0.030							
In ethyl alcohol :	about 44							
in methyl alcohol:	57.5							
In ether:	very soluble							
In benzene and ligroin :	slightly soluble							
Health Hazard : Toxic on ingestion, inhalation, or skin absorption. Irritating to the mucous membranes.								12, 29

Diphenylamine (page 2)

Safety Classifications :

OSM: Listed **as** substantially inert. Presents no particular fire or toxic hazard as used in Ordnance establishments.

Fire and Explosion Hazard : Dangerous ; when heated to decomposition emits highly toxic fumes. Can react with oxidizing materials. Combustible. **12**

To fight fire use water, **CO₂**, dry chemicals, or CCl₄. **67, 75**

Heat of Combustion, Kcal./mole at 20°C and 1 atm. : **1536.2** **1**

Specific Heat, cal. (15°)/g./°C, solid at **26°C** : **0.337** **1**

liquid at **53°C**: **0.464**

Flash Point, °F (closed cup) : **307** **12, 67**

Autoignition Temperature, °F : **846** **12, 67**

Electrostatic Sensitivity :

Use in Pyrotechnics: **as a stabilizer for nitrocellulose**

Additional References :

- I) L. Médard, Mém. artillerie franç, **28,478 (1954)**

ETHYLCELLULOSE

(Cellulose Ethyl Ether)

Refs.

Formula : $[\text{C}_6\text{H}_{10-x}\text{O}_5-x(\text{OC}_2\text{H}_5)_x]_n$

where x = no. of (OC_2H_5) groups and n = degree of polymerization

Specification No. :

MIL-E-10853B

The spec. covers 46.8–48.5% ethoxyl content or x = approximately 2.4–2.5, and lists two classes which vary in viscosity, ethoxyl content, ash content, and granulation : class I, 46.8–48.5% ; class II, 47.1–48.1%.

Molecular Weight :

variable high

Crystalline Form :

(specification) amorphous granules

Color :

white

Density, g./ml. :

(solid) 1.09-1.17

60

Coefficient of Thermal Expansion :

—

Heat of Formation :

—

Free Energy of Formation :

—

Entropy :

—

Melting Point :

513°K + (240 ± °C)

12

Ethyl cellulose with 48% ethoxyl content softens at 425–435°K

69

(152–162°C)

Heat of Fusion:

—

Boiling Point :

—

Transition Point :

Second order transition temperature, °C :

43

59

Heat of Sublimation :

—

Heat Content or Enthalpy:

—

Heat Capacity :

—

Decomposition Temperature :

—

For DTA and TGA see Ref. 33

Decomposition Products :

—

Vapor Pressure:

—

X-Ray Crystallographic Data :

—

Hygroscopicity :

—

Solubility Data (for 47% ethoxyl content) : Soluble in ethyl acetate, ethylene, dichloride, benzene, toluene, xylene, butyl acetate, acetone, methanol, ethanol and CCl_4 .

29

Health Hazard :

none mentioned

Safety Classifications :

OSM :

not listed

ICC :

not listed

Ethylcellulose (page 2)

Fire and Explosion Hazard: Combustible when exposed to heat or flame by chemical reaction with oxidizing agents. Flammability varies with ethoxyl content.	12, 60
Ignition Temperature of Dust Cloud, °C: 320	26
Burning Behavior: First melts and drips and drippings continue to bum. The flame is yellow with blue edges.	60
Commercial Types : A number of types of ethylcellulose are commercially available. These range from 44.5 to 49.0 + in ethoxyl content and from very low to highly viscous materials (5% concentration from 3 to 5000 + centipoises)	69
Electrostatic Sensitivity, minimum energy required for ignition of dust cloud by electric sparks (millijoules) : 10	26
Use in Pyrotechnics: as a binding agent and retardant	12
Additional References :	
1) "Cellulose and Cellulose Derivatives," E. Ott et al., Eds., Interscience Publishers, Inc., New York (1954)	

FERRIC OXIDE, Fe ₂ O ₃			Refs.
(Iron Oxide, Burned Ochre, Indian Red Rouge, Venetian Red, Red Chalk, Red Earth, Red Hematite, Red Stone, Persian Red, Persian Gulf Oxide, Colcothar, Iron Sesquioxide)			1, 11, 16, 29
Percent Oxygen :	30.06		
Specification No. :	JAN-1-706		
The specification covers class 1, coarse, and class 2, fine.			
Molecular Weight :	159.70		
Crystalline Form :	hexagonal		1
Color :	reddish-brown to black		1
Density, g./ml. :	(solid) 5.24		
Coefficient of Thermal Expansion, linear :	7×10^{-6}		54V13
cubic :	4×10^{-5}		
See also Addnl. Ref. 2			
Heat of Formation, Kcal./mole :	-196.5		1, 9
See Table a			
Free Energy ¹ of Formation, Kcal./mole :	-177.9		8, 9
See Table a			
a. HEAT AND FREE ENERGY OF FORMATION OF Fe₂O₃ (hematite, β, γ)			2
T, °K	ΔH (cal./mole)	ΔF° (cal./mole)	
298.16	-196,800 ($\pm$ 1300)	-177,400 ($\pm$ 1500)	
400	-196,400	-170,800	
500	-195,800	-164,500	
600	-195,200	-158,300	
700	-194,500	-152,200	
800	-193,800	-146,200	
900	-193,000	-140,300	
950	-192,800	-137,400	
950	-192,600	-137,400	
1000	-192,600	-134,500	
1033	-193,100	-132,600	
1033	-193,100	-132,600	
1050	-193,000	-131,600	
1050	-193,000	-131,600	
1100	-193,000	-128,700	
1179	-193,000	-124,100	
1179	-193,400	-124,100	
1200	-193,300	-122,800	
1300	-193,000	-117,000	

Ferric Oxide, Fe₂O₃ (page 2)

T, °K	A H (cal./mole)	A F° (cal./mole)
1400	-192,600	-111,100
1500	-192,400	-105,300
1600	-192,100	-99,500
1674	-191,900	-95,200
1674	-192,100	-95,200
1700	-192,100	-93,700
1800	-191,700	-88,000

Phase Changes of Metal

T.P., 1033°K ; Δ H = 0 (Curie point)

T.P., 1179°K ; A H = 210 cal./g.-atom

T.P., 1674°K ; A H = 110 cal./g.-atom

Free Energy Equations :

Reaction	Range of Validity, °K
1) $2\text{Fe}(\alpha) + 3/2 \text{O}_2(\text{g}) = \text{Fe}_2\text{O}_3(\text{hematite})$ $\Delta F_T^\circ = -200,000 - 13.84T \log T - 1.45 (10^{-3}T^2) + 1.905 (10^5T^{-1}) + 108.28T$	298.16-950
2) $2\text{Fe}(\alpha) + 3/2 \text{O}_2(\text{g}) = \text{Fe}_2\text{O}_3(\beta)$ $\Delta F_T^\circ = -202,960 - 42.641' \log T + 7.85 (10^{-3}T^2) + .13 (10^5T^{-1}) + 188.48T$	950-1033
3) $2\text{Fe}(\beta) + 3/2 \text{O}_2(\text{g}) = \text{Fe}_2\text{O}_3(\beta)$ $\Delta F_T^\circ = -196,760 - 10.27T \log T + .75 (10^{-3}T^2) - .30 (10^5T^{-1}) + 92.86T$	1033-1050
4) $2\text{Fe}(\beta) + 3/2 \text{O}_2(\text{g}) = \text{Fe}_2\text{O}_3(\gamma)$ $\Delta F_T^\circ = -193,200 - .39T \log T - .13 (10^{-3}T^2) - .30 (10^5T^{-1}) + 59.961T$	1050-1179
5) $2\text{Fe}(\gamma) + 3/2 \text{O}_2(\text{g}) = \text{Fe}_2\text{O}_3(\gamma)$ $\Delta F_T^\circ = -202,540 - 25.95T \log T + 2.87 (10^{-3}T^2) - .30 (10^5T^{-1}) + 142.851T$	1179-1674
6) $2\text{Fe}(\delta) + 3/2 \text{O}_2(\text{g}) = \text{Fe}_2\text{O}_3(\gamma)$ $\Delta F_T^\circ = -192,920 - .85T \log T - .13 (10^{-3}T^2) - .30 (10^5T^{-1}) + 61.21T$	1674-1800

Entropy, cal./deg./mole at 298.16°K:

21.5

See Table b

Melting Point:

1838°K (1565°C)

Heat of Fusion:

—

Boiling Point:

—

Heat of Vaporization:

—

Transition Point:

$\alpha \xrightarrow{950^\circ\text{K}} \beta \xrightarrow{1050^\circ\text{K}} \gamma$

Heat of Transition, cal./mole:

$\alpha \text{ to } \beta = 160; \beta \text{ to } \gamma = 0$

Heat of Sublimation:

—

b. HEAT CONTENT AND ENTROPY OF Fe₂O₃(c)
 (Base, α -crystals at 298.15°K)

4

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	2750	7.91	1050 (y) . . .	25,820	41.31
500	5770	14.64	1100	27,500	42.87
600	9010	20.54	1200	30,870	45.80
700	12,460	25.85	1300	34,250	48.51
800	16,130	30.75	1400	37,650	51.03
900	20,030	35.34	1500	41,070	53.39
950 (a) . . .	22,060	37.54	1600	44,540	55.63
950 (β) . . .	22,220	37.71	1700	48,100	57.79
1000	24,020	39.55	1800	51,880	59.95
1050 (β) . . .	25,820	41.31			

$\text{Fe}_2\text{O}_3(\alpha):$
 Enthalpy: $H_T - H_{298.15} = 23.49T + 9.30 \times 10^{-5}T^2 + 3.55 \times 10^{-8}T^3 - 9021$
 (0.1 percent; 298-950°K)

Heat Capacity: $C_p = 23.49 + 18.60 \times 10^{-5}T - 3.55 \times 10^{-8}T^2$

$\text{Fe}_2\text{O}_3(\beta):$
 Enthalpy: $H_T - H_{298.15} = 36.00T - 11,980$ (0.1 percent; 950-1050°K)

$\text{Fe}_2\text{O}_3(\gamma):$
 Enthalpy: $H_T - H_{298.15} = 31.71T + 0.88 \times 10^{-5}T^2 - 8446$
 (0.1 percent; 1050-1800°K)

Heat Capacity: $C_p = 31.71 + 1.76 \times 10^{-5}T$

Heat Capacity, cal./deg./mole: (solid) $\alpha = 25.0$
 $\beta = 36.0$

Decomposition Temperature, °K: 1730

See also Ref. 54V13

Decomposition Products: (high temp.) $\text{Fe}_3\text{O}_4 + \text{O}_2$

Vapor Pressure: Difficult to vaporize. Contradictory data in the literature.

X-Ray Crystallographic Data:

	System	Space Group	a	Axial Angle	Molecules/ Unit Cell
(hematite)	hexagonal	D _{3d} ⁶	5.42	$\alpha = 55^\circ 17'$	2
(magnetic)	cubic		8.30		

Hygroscopicity: —

Solubility Data: Insoluble in water; soluble in acids.

Health Hazard: none reported

M.A.C., mg./m.³ (for fumes): 15

9

4

8

Addnl. Ref. 3

44V59B

1

50V7

25

Ferrie Oxide, Fe₂O₃ (page 1)

Safety Classifications:	none listed
Fire and Explosion Hazard:	none listed
Electrostatic Sensitivity:	—
Use in Pyrotechnics:	as an oxidizer

Additional References:

- 1) "Health Hazards Associated with Welding," F. Hutchinson, Heating and Ventilating **41**, 73 (1944)
- 2) C.A. **45**, 9978 (1951) refers to Proc. Indian Acad. Sci. **33A**, 245-249 (1951) where data are given.
- 3) C.A. **36**, 4400 (1942)

FERROSPERRIC OXIDE, Fe_3O_4			Refs.
(Iron (II, III) Oxide, Black Iron Oxide, Magnetite, Triiron Tetroxide, Magnetic Iron Oxide, Ethiops Iron, Lodestone)			1, 2, 9
Percent Oxygen:	27.64		
Specification No.:	JAN-1-2'75		
Molecular Weight:	231.55		
Crystalline Form:	cubic		1
Color:	black to red-black		1
Density, g./ml.:	(solid) 5.18		1
Coefficient of Thermal Expansion, linear, 17-50 °C:	95.4×10^{-6}		54V13
(magnetite) cubic, 17-50 °C:	29×10^{-6}		
Heat of Formation, Kcal./mole at 298°K:	-267.0		1, 9
See Table a			
Free Energy of Formation, Kcal./mole at 298°K:	-242.4		1, 9
See Table a and Free Energy Equations			

a. HEAT AND FREE ENERGY OF FORMATION OF Fe_3O_4 (magnetite, β , 1)

T, °K	ΔH (cal./mole)	ΔF° (cal./mole)
298.16	-267,800 (± 1000)	-243,200 (± 1200)
400	-267,200	-234,900
500	-266,300	-226,900
600	-265,300	-219,100
700	-264,000	-211,500
800	-262,300	-204,100
900	-260,500	-197,000
900	-260,500	-197,000
1000	-260,800	-189,900
1033	-261,700	-187,600
1033	-261,700	-187,600
1100	-261,700	-182,800
1179	-261,700	-177,100
1179	-262,300	-177,100
1200	-262,200	-175,600
1300	-261,700	-168,400
1400	-261,300	-161,200
1500	-261,000	-154,100
1600	-260,800	-147,000
1674	-260,700	-141,700
1674	-261,000	-141,700
1700	-261,100	-139,800
1800	-261,100	-132,700
1803	-261,100	-135,500
1803	-272,200	-132,500
1870	-272,200	-127,200
1870	-239,200	-127,300
1900	-239,000	-125,800
2000	-238,200	-119,800

Ferrosoferric Oxide, Fe₃O₄ (page 2)

Phase Changes of Metal

T.P., 1033°K; ΔH = 0 (Curie point)

T.P., 1179°K; ΔH = 210 cal./g.-atom

T.P., 1674°K; ΔH = 110 cal./g.-atom

M.P., 1803°K; ΔH = 3700 cal./g.-atom

Free Energy Equations :

Reaction	Range of Validity, °K
1) 3Fe (α) + 2O ₂ (g) = Fe ₃ O ₄ (magnetite)	298.16-900
ΔF _T ^o = -268,310 + 5.87T log T - 12.45 (10 ⁻³ T ²) + .245 (10 ⁵ T ⁻¹) + 73.11T	
2) 3Fe (α) + 2O ₂ (g) = Fe ₃ O ₄ (β)	900-1033
ΔF _T ^o = -272,300 - 54.27T log T + 11.65 (10 ⁻³ T ²) + .245 (10 ⁵ T ⁻¹) + 233.52T	
3) 3Fe (β) + 2O ₂ (g) = Fe ₃ O ₄ (β)	1033-1179
ΔF _T ^o = -262,990 - 5.71T log T + 1.00 (10 ⁻³ T ²) - .40 (10 ⁵ T ⁻¹) + 89.19T	
4) 3Fe (γ) + 2O ₂ (g) = Fe ₃ O ₄ (β)	1179-1674
ΔF _T ^o = -276,990 - 44.05T log T + 5.50 (10 ⁻³ T ²) - .40 (10 ⁵ T ⁻¹) + 213.52T	
5) 3Fe (δ) + 2O ₂ (g) = Fe ₃ O ₄ (β)	1674-1803
ΔF _T ^o = -262,560 - 6.40T log T + 1.00 (10 ⁻³ T ²) - .40 (10 ⁵ T ⁻¹) + 91.05T	
6) 3Fe (l) + 2O ₂ (g) = Fe ₃ O ₄ (β)	1803-1874
ΔF _T ^o = -275,280 - 8.74T log T + 1.00 (10 ⁻³ T ²) - .40 (10 ⁵ T ⁻¹) + 104.84T	
7) 3Fe (l) + 2O ₂ (g) = Fe ₃ O ₄ (l)	1874-2000
ΔF _T ^o = -257,240 - 26.89T log T + 1.00 (10 ⁻³ T ²) - .40 (10 ⁵ T ⁻¹) + 155.46	

Entropy, cal./deg./mole at 298°K :

See Table b

Melting Point :

Heat of Fusion, cal./mole :

Boiling Point :

Heat of Vaporization :

Transition Point :

Heat of Transition, cal./mole :

Heat of Sublimation :

900°K (627°C)
α → β
0.0

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	3990	11.48	1100	40,150	62.81
500	8320	21.12	1200	44,950	66.99
600	13,060	29.75	1300	49,750	70.83
700	18,340	37.88	1400	54,550	74.39
800	24,260	45.77	1500	59,350	77.70
900 (α) . . .	30,550	53.18	1600	64,150	80.80
900 (β) . . .	30,550	53.18	1700	68,950	83.71
1000	35,350	58.24	1800	73,750	86.45

Ferrosoferric Oxide, Fe_3O_4 (page 3)

	$\text{Fe}_3\text{O}_4 (\gamma)$:	2
Enthalpy: $H_T - H_{298.15} = 21.88T + 24.10 \times 10^{-3}T^2 - 8666$ (0.5 percent; 298-900°K)		
Heat Capacity: $C_p = 21.88 + 48.20 \times 10^{-3}T$		
	$\text{Fe}_3\text{O}_4 (\beta)$:	
Enthalpy: $H_T - H_{298.15} = 48.00T - 12,650$ (0.1 percent; 900-1800°K)		
Heat Capacity, cal./deg./mole :	(solid) β , 48.00	4
Decomposition Temperature, °K :	2060 $\pm$ 30	8
Stable at red heat. Begins to decompose in a current of N at over 1300°.		54
Decomposition Products :	—	
Vapor Pressure :	—	
X-Ray Crystallographic Data :		
<i>System</i> cubic	<i>Space Group</i> O_h^1	<i>a</i> 8.37
		<i>Molecules/Unit Cell</i> 8
Solubility Data : Slightly soluble in acid; insoluble in alcohol and ether.		1 50V7
Health Hazard :	none reported	
M.A.C., mg./m. ³ (for fumes) :	15	25
Safety Classifications:	—	
Fire and Explosion Hazard:	—	
Electrostatic Sensitivity :	—	
Use in Pyrotechnics:	as an oxidizer	
Additional Reference :		
I) "Health Hazards Associated with Welding," F. Hutchinson, Heating and Ventilating 41, 73 (1944)		

FERROUS SULFIDE, FeS (Iron Monosulfide, Iron Proto-Sulfide, Pyrrhotite)			Refs.		
Specification No. :	JAN-F-279				
The spec. covers one grade and two classes. Class A requires a min. of 99.9% through a No. 100 Standard Sieve and Class R requires that the FeS be furnished in pieces capable of passing through a sieve having openings 1-in. square.					
Molecular Weight:	87.92				
Crystalline Form :	hexagonal		1		
Color :	black-brown (colorless when pure)		1, 79		
Density, g./ml. :	(solid) 4.84		1		
Coefficient of Thermal Expansion (pyrrhotite) at 40°C :					
In direction of principal axis:		.00000235	54		
Perpendicular :		.00003120			
Heat of Formation, Kcal./mole at 298°K :	(c) α , -22.72		1, 9		
	β , -21.35		1, 9		
Free Energy of Formation, Kcal./mole at 298°K :	(c) α , -23.32		1, 9		
Entropy, cal./deg./mole at 298°K :	16.1		1, 9		
See following table					
Melting Point:	1468°K (1195°C)		4, 7		
Heat of Fusion, cal./mole :	p , 5000		7		
	y , 7730		4		
Boiling Point:	decomposes		1		
Transition Point :	$\alpha \xrightarrow{411^\circ\text{K}} \beta \xrightarrow{598^\circ\text{K}} \gamma$				
Heat of Transition, cal./mole :	$\alpha \xrightarrow{570^\circ\text{K}} \beta \xrightarrow{120^\circ\text{K}} \gamma$		4		
			4		
T, °K	$H_T - H_{298,15}$ cal./mole	$S_T - S_{298,15}$ cal./deg. mole	T, °K	$H_T - H_{298,15}$ cal./mole	$S_T - S_{298,15}$ cal./deg. mole
350	710	2.19	1100	12,680	21.35
500	1470	4.21	1200	14,150	22.63
411 (c)	1640	4.63	1300	15,680	23.86
411 (β)	2210	6.02	1400	17,260	25.03
500	3760	9.43	1468 (γ)	18,350	25.79
598 (β)	5460	12.53	1468 (l)	26,080	31.05
598 (γ)	5580	12.73	1500	26,620	31.42
600	5610	12.79	1600	28,320	32.51
700	7020	14.96	1700	30,020	33.54
800	8430	16.84	1800	31,720	34.51
900	9840	18.50	1900	33,420	35.43
1000	11,250	19.99	2000	35,120	36.31

Ferrous Sulfide, FeS (page 2)

		FeS (α) :	
Enthalpy :	$H_T - H_{298.15} = 5.19T + 18.20 \times 10^{-5}T^2 - 2721$	(0.8 percent; 298–411°K)	
Heat Content :	$C_p = 6.19 + 26.40 \times 10^{-5}T$		
		FeS (β) :	
Enthalpy :	$H_T - H_{298.15} = 17.40T - 4944$	(0.1 percent; 411–598°K)	
		FeS (γ) :	
Enthalpy :	$H_T - H_{298.15} = 12.20T - 1.19 \times 10^{-5}T^2 - 2138$	(0.3 percent; 598–1468°K)	
Heat Content :	$C_p = 12.20 + 2.38 \times 10^{-5}T$		
		FeS (l) :	
Enthalpy :	$H_T - H_{298.15} = 17.00T + 1120$	(0.1 percent; 1468–2000°K)	
Heat Capacity, cal./deg./mole :		(α) 13.1 (β) 17.4 (liquid) 17.00	1, 9
Decomposition Temperature:	In a vacuum, dissociation starts at about 1100°C and is complete at 1600°C.		79V2
Decomposition Products:	Fe + S		
Vapor Pressure :	—		
X-Ray Crystallographic Data :			
System	Space Group	a	c
hexagonal	C_{6v}	3.43	5.79
			Molecules/Unit Cell
			2
Hygroscopicity :	—		1
Solubility Data :	In water : .00062 g./100 ml. at 18°C. Soluble in acids with evolution of H ₂ S. Insoluble in ammonia.		1
Health Hazard :	slight (ordinary temp.)		12
Safety Classifications :			
OSM :	not listed		
ICC :	not listed		
Fire and Explosion Hazard :	Dangerous when heated to decomposition, due to the highly toxic fumes of oxides of sulphur. On contact with moist acids poisonous hydrogen sulphide evolves which can form explosive mixtures with air. May react violently with powerful oxidizers.		12
Use in Pyrotechnics:	as a fuel		

GRAPHITE

(Plumbago, Black Lead, Mineral Carbon,
Silver Lead, Carburet of Iron)

Refs.

Graphite occurs naturally as a mineral and is also made artificially by heating carbon, usually coal, in an electric furnace. Natural graphites are of three general types: flake, crystalline (plumbago), and amorphous. The artificial product is purer than the natural. Graphite is marketed in a number of grades based on purity, electrical resistance, and fineness. In an inert atmosphere graphite can be kept at 3000°C without change, but in air combines with oxygen above 600°C. The hardness of natural graphite is less than that of talc, which is 1 on Moh's scale. Graphite is a good conductor of heat and electricity.

16, Addnl.
Ref. 1

Specification No. :

JAN-G-155

The spec. covers four grades: grades 1 and 3 are manufactured; 2 and 4 are natural. They differ in purity, the natural being less pure and containing up to 6% max. of silica vs. 0.6% for the manufactured material. Natural graphite is used in pyrotechnics.

Molecular Weight :	12.011	
Crystalline Form :	hexagonal	1
Color :	black	1
Density, g./ml. :	(solid) 2.25	P
Coefficient of Thermal Expansion, linear at 40°C :	7.86×10^{-6}	1, 63
Heat of Formation, Kcal./mole at 298°K :	(gas) -170.890	5
Free Energy of Formation, Kcal./mole at 298°K :	(gas) -160.040	5
Entropy, cal./deg./mole at 298°K :	(gas) 37.76 (solid) 1.37	3, 4, 5 5
See following table		
Melting Point:	sublimes	
Heat of Fusion, cal./mole:	8000	Addnl. Ref. 4
Boiling Point :	4000°K (3727°C)	6
Transition Point (sublimation temp.)	4620°K (4347°C)	1
Heat of Sublimation, Kcal./mole, to ideal		
monatomic gas :	170	5
to diatomic and triatomic gas :	200	
Heat Content or Enthalpy, cal./mole at 298°K :	(solid) 251	
See equation below table	(gas, ideal)	
	monatomic, 1559	5
	diatomic, 2096	
	triatomic, 2541	

Graphite (page 2)

HEAT CONTENT AND ENTROPY OF C (graphite)
(Base, crystals at 298.15°K)

4

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	250	0.72	1800	7330*	7.78
500	570	1.43	1900	7920	8.10
600	950	2.12	2000	8530	8.41
700	1370	2.77	2100	9130	8.70
800	1830	3.38	2200	9740	8.99
900	2320	3.95	2300	10,350	9.26
1000	2820	4.48	2400	10,970	9.52
1100	3340	4.98	2500	11,600	9.78
1200	3880	5.48	2750	13,170	10.38
1300	4430	6.89	3000	14,770	10.93
1400	4990	6.30	3250	16,390	11.45
1500	5560	6.70	3500	18,020	11.93
1600	6150	7.08	3750	19,660	12.39
1700	6740	7.44	4000	21,310	12.81

Enthalpy : $H_T - H_{298.15} = 4.03T + 0.67 \times 10^{-5}T^2 + 2.04 \times 10^{-5}T^{-1} - 1936$
(8.0 percent; 298-2500°K)

Heat Capacity : $C_p = 4.03 + 1.14 \times 10^{-5}T - 2.04 \times 10^{-5}T^{-2}$

Heat Capacity, cal./deg./mole : (solid) 2.07 (gas) 4.98

See equation below table

Decomposition Temperature : —

Decomposition Products : —

Vapor Pressure : —

Press. mm.	1	10	40	100	400	760
Temp. °C	3586	3946	4196	4373	4660	4827

X-Ray Crystallographic Data :

System	Space Group	a	c	Molecules/Unit Cell
hexagonal	D _{6h} ¹	2.455	6.99	4

Hygroscopicity : —

Solubility Data : Insoluble in water, acids and alkalies. Soluble in molten iron.

Health Hazard: Dust can irritate eyes.

Safety Classifications:

OSM :

not listed

ICC :

not listed

Fire and Explosion Hazard: —

Graphite (page 3)

Electrostatic Sensitivity :

Heat of Combustion, Kcal./g. :

7.900

Use in Pyrotechnics:

as a lubricant; to improve
bonding under pressure

1

Additional References :

- 1) "Industrial Carbon," C. L. Mantell, D. Van Nostrand Co., Princeton, N. J. (1946)
- 2) "The Specific Heat of Graphite from 13° to 300°K," W. De Sorbo and W. W. Tyler, Chem. Physics **21**, 1660 (1953); see also Ref. 63
- 3) Ref. 64
- 4) "Vapor Pressure and Heat of Vaporization of Graphite," A. L. Marshall and F. J. Norton, J. Am. Chem. Soc. **55**, 432 (1933)
- 5) For X-Ray structure see also "The Synthesis of Diamond," H. T. Hall, J. Chem. Ed. **38**, 484 (1961)

GUM ARABIC

(Gum Preservative, Gum Acacia)

Refs.

Gum arabic is the dried **gummy** extraction obtained from acacia trees. The **gum** is produced **when** the trees are in an unhealthy condition. Most of the **gum** comes from the Sudan and West Africa. Today tapping is widely used. The **gum** exudes **as** droplets or "tears" which gradually harden on exposure to the atmosphere. These "tears" are 0.75 to 3 in. in diameter. After the "tears" are removed the tree continues to exude **gum** from the wound. For the better grades the cleaned **gum** is hand picked to remove extraneous material. Some **gum** is bleached by exposure to the sun for several weeks. The gum is available in several **grades**: natural, cleaned and sifted, bleached and dust.

16, 23, 29, 61

In addition **to** the more common names of **gum** arabic, **gum** preservative, and gum acacia, other names relating to the color or grade or to the local area are used **so** that there is a great deal of confusion concerning the relationship among the name, the actual **gum** and the species of acacia from which the **gum** is derived. **As usually** shipped the gum contains about 15% moisture. Its aqueous solution is slightly acid.

Gum arabic has been used **as** an adhesive since ancient times. It is a **good** emulsifying agent.

See also Addnl. Refs. 1, 2, 3

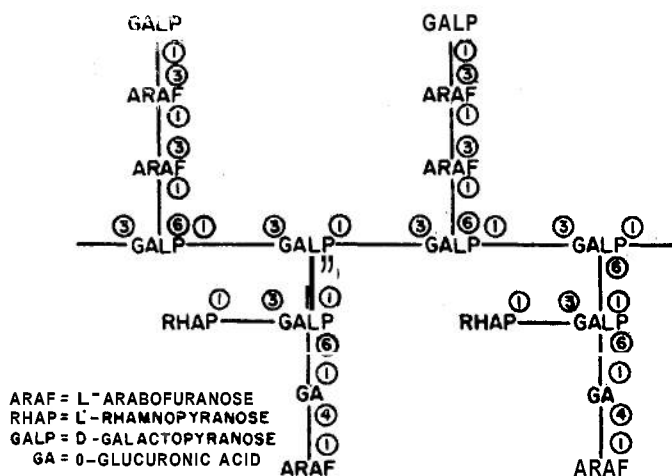
Specification:	JJJ-G-821	
Molecular Weight: Variable high ; probably in the range of 100,000 to 200,000. See Structure below		
Density, g./ml.:	1.3-1.4 1.35-1.49	1 29
Vapor Pressure:	—	
X-Ray Crystallographic Data :	—	
Hygroscopicity : Poor resistance to water.		29, 60
Solubility Data: Soluble in hot or cold water; oil and most organic solvents; aqueous alcohol up to about 60% alcohol; glycerol and propylene glycol.		1, 23, 29
Safety Classifications:		
OSM:	not listed	
ICC:	not listed	
Health Hazard : When injected intravenously may cause allergic reactions, kidney and liver damage.		29
Fire and Explosion Hazard:	combustible	
Electrostatic Sensitivity :	—	
Chemical Structure :		
Gum arabic from different sources contains the same sugars, but their proportions vary considerably, as shown by the following table:		

Gum Arabic (page 2)

MOLAR RATIO OF CARBOHYDRATE COMPONENTS IN VARIOUS ACACIA GUMS

Gum Source	Approximate Molar Ratio			
	D-Galactose	L-Arabinose	L-Rhamnose	D-Glucuronic Acid
Gum arabic	3	3	1	1
Acacia mollissima	5	6	1	1
Acacia cyanophylla	11	2	5	5
Acacia karroo	25	22	1	6
Acacia verec	4	2	1	1
Acacia pycnantha	65	27	2	4

A number of complex structures have been proposed not only for gum from different sources but also from the same source. Hydrolysis of gum arabic yields four different sugars, as shown in the table above, which together make up the basic gum arabic molecule. Because the proportions of these sugars vary with the source of the gum, no single formula can have any real significance. The following proposed structure indicates the complex nature of the gum:



PROPOSED STRUCTURE FOR GUM ARABIC

Use in Pyrotechnics :

as a fuel, bonding agent,
adhesive, and retardant

Additional References :

- 1) Ref.70
- 2) "Natural Plant Hydrocolloids," Ind. & Eng. Chem., Eds., Advances in Chemistry Series, No. 11, American Chemical Society, Washington, D.C.(1954)
- 3) "The Structure of Acacia Sundra Gum — Part I. Nature of the Sugars Present and Structure of the Aldobiuronic Acid," S. Mukherjee and A. N. Shivastava. J. Am. Chem. Soc. 80,2536 (1958)

GUM TRAGACANTH

Gum tragacanth is the dried **gummy exudate** obtained from several varieties of the shrub-like plants of the Astragalus family, which **grow** in the semi-desert and mountainous areas of Turkey, Iran, and Syria. The **gum** exudes spontaneously and hardens on exposure to the air either in the form of short (2-4 in.) ribbons which are flat, flexible and opaque, or in thick brittle flakes (0.5-2 in.), depending on the particular species of plant. The supply is increased by making incisions in the shrubs. The **gum** is sorted into five grades; the best grades being the lightest colored of the longest ribbons or largest flakes.

Chemically, gum tragacanth is a complex mixture of polysaccharides. On hydrolysis D-galacturonic acid, D-galactose, L-fucose, D-xylose, and L-arabinose are obtained. Gum tragacanth is about 60-70% insoluble in water, but swells to form a gel which is regarded as bassorin ($C_{11}H_{20}O_{10}$). The water soluble portion which gives a colloidal hydrosol with water is called tragacanthin. It consists of a ring of three molecules of glucuronic acid and 1 molecule of arabinose with a side chain of two molecules of arabinose.

Gum tragacanth in solution has the properties of a partially cross-linked polymer, in that a small portion is soluble while the greater portion remains as a swollen gel or gel-like dispersion. When properly preserved, gum tragacanth forms stable solutions over long periods of time in either cold or warm storage.

A study of the infrared spectra of a wide variety of gums showed that the different samples of any one type of gum have essentially the same type of spectrum. Tragacanth shows a strong carbonyl absorption at about 5.75μ . The differences among the various infrared spectra are sufficiently definite to serve as a means of identification and classification.

An analysis of a representative sample of gum tragacanth shows the following percentages :

Moisture	10	Ash	3
Starch	3	Tragacanth	70
		(swelling part)	
Cellulose	4	Araban	10
		(soluble part)	

Viscosity is the most important property in evaluating gum tragacanth. It is the most direct measure of the uniformity and quality of the gum. To obtain maximum viscosity, the gum is crushed and soaked overnight. The dispersion is then stirred for 15-30 minutes. For powdered gums, it is best to disperse the gums in small amounts of ethanol or glycerol before the addition of water. Heat is not recommended for faster dissolution or increased viscosity. Viscosity is also decreased by adding acid, alkali, and NaCl.

Specification No. :

JAN-G-96

Solubility Data : Partly soluble in water. Films cast from aqueous solutions of gum tragacanth are unaffected by organic solvents such as acetone, ethanol, CCl_4 , xylene, and toluene. When painted with solutions of basic or neutral lead acetate, these films also become insoluble in water.

Health Hazard : Nontoxic. Used in pharmaceutical compounding.

Safety Classifications :

OSM :

not listed

ICC :

not listed

Fire and Explosion Hazard:

combustible

Use in Pyrotechnics:

fuel ;bonding agent

Additional References :

- 1) "Natural Plant Hydrocolloids," Ind. & Eng. Chem., Eds., Advances in Chemistry Series No. 11, American Chemical Society, Washington, D.C. (1954)

Refs.

23, 29, til. 70
Addnl. Ref. 1

23

23

29

23

29

Specification No. :	JAN-H-257	
Molecular Weight :	284.80	
Crystalline Form :	monoclinic or rhombic prisms	1
Color:	colorless *	1
Density, g./ml. :	(solid) 2.044 (rhomb.)	1
Coefficient of Thermal Expansion :	—	
Heat of Formation, Kcal./mole at 25°C :	41.3 ± 0.3	Addnl. Ref. 1
Free Energy of Formation, Kcal./mole at 298°K :	+3 ± 1.0	Addnl. Ref. 2
Entropy, cal./deg./mole at 298°K :	62.20	Addnl. Ref. 2
Melting Point :	500°K (227°C)	1
Heat of Fusion :	—	
Boiling Point:	599°K (326°C)	1
Transition Point, rhombic to triclinic : triclinic to cubic:	316.7°K (43.6°C) 345°K (72°C)	Addnl. Ref. 8 76
Heat of Sublimation:	—	
Heat Content or Enthalpy :	—	
Heat Capacity, cal./deg./mole at 298°K :	(solid) 48.11	Addnl. Ref. 2
Decomposition Temperature: For DTA see Addnl.	Ref. 4	
Decomposition Products :	—	
Vapor Pressure :		
Press. mm.	1 10 40 100 400 760 M.P.	
Temp. °C	114.4 166.4 206.0 235.6 283.5 309.4 230	1
X-Ray Crystallographic Data :		
System	Space Group	Molecules/ Unit Cell
monoclinic	C _{2h} <i>a</i> 8.07 <i>b</i> 3.84 <i>c</i> 16.61 8.10 3.86 16.68	2 1 85
Axial Angle	β = 116°52'	
Hygroscopicity :	—	
Solubility Data : In water :	insoluble	1
In alcohol:	insoluble cold, very soluble hot	
In benzene:	soluble hot	
In ether:	very slightly soluble	
Health Hazard: May produce mild skin irritation on prolonged contact. OSM states that it presents no particular toxic hazard as used in Ordnance establishments. Severly toxic on ingestion or inhalation.		29, 14, 93
M.A.C., mg./m. ³ :	0.5	17

Hexachlorobenzene, C_6Cl_6 (page 2)

Safety Classifications:

OSM : Inert and **presents no** particular **fire** hazard in Ordnance establishments.

ICC : **No** shipping label required.

Manufacturing ~~Chemists Assn.~~ requires **a** warning label.

22

Fire and Explosion **Hazard:** Slight when exposed **to** heat or flame. Flash point **468°F.** Dangerous when heated to decomposition **because** of emission of highly toxic fumes. **To** fight **fire use** CO_2 , dry chemical, or ~~carbon~~ tetrachloride.

12

Heat of Combustion, **at 20°C and 1 atm.,** Kcal./mole.

(water liquid) :

509.0

1

25°, cal./g. (water liquid) :

1995.3

Addnl. Ref. 1

Electrostatic Sensitivity :

Use in Pyrotechnics:

as a color intensifier
and chlorine donor in
white smokes

17

Additional References :

- 1) "Heats of Combustion of Some Organic Compounds Containing Chlorine," G. C. Sinke and D. R. Stull, J. Phys. Chem. **62,397 (1958)**
- 2) "The Heat Capacities of Hexachlorobenzene and Pentachlorophenol from 15° to 300°K," D. L. Hildenbrand et al., J. Phys. Chem. **62, 958 (1958)**
- 3) "The Vapor Pressures, Latent Heats of Sublimation and Transition Points of Solid Hexachloroethane," K. J. Ivin and F. S. Dainton, Trans. Faraday Soc. **43, 32 (1947)**
- 4) "Pre-Ignition and Ignition Reactions of the Pyrotechnic System Zn - C_6Cl_6 - $KClO_4$," S. Gordon and C. Campbell, Reinhold Publishing Company, New York **(1955)**

HEXACHLOROETHANE, $\text{CCl}_3 \cdot \text{CCl}_3$			Refs.
(Carbon Hexachloride, Perchlorethane Carbon Trichloride)			1, 12
Specification No. :	JAN-H-235		
The spec. covers one grade and two classes : class a, unground, and class b, ground.			
Molecular Weight :	286.76		
Crystalline Form :	rhombic, tablets from alcohol or ether rhombic, triclinic or cubic		1 12
Color :	colorless to yellowish-white		1
Density, g./ml. :	(solid) .091		1
Coefficient of Thermal Expansion:	—		
~~Heat~~ of Formation, Kcal./mole at 298°K :	(gas) -48		9
Free Energy of Formation, Kcal./mole at 298°K :	—		
Entropy, cal./deg./mole at 298°K :	91.97		Ad Int. Ref. 3
See table below			
Melting Point :	(sublimes) 186.6°K (-86.5°C)		12
Heat of Fusion, Kcal./mole :	—		
Boiling Point :	(sublimes) 457.5°K (184.4°C)		9
~~Heat~~ of Vaporization, cal./g. :	approx. 46		52V1
Transition Point :	sublimes at 457.6°K (184.5°C) rhombic—triclinic 43.6°K (-229.5°C) triclinic→cubic 72°K (-201°C)		9
Heat of Sublimation, Kcal./mole :	12.2		9
Heat Content or Enthalpy:			
See table below			
Heat Capacity, cal./deg./mole :	(solid) 41		
See table below			
ENTROPY . ENTHALPY . AND HEAT CAPACITY			Addnl. Ref. 3
Temp. °K	Entropy cal./deg./mole	Enthalpy cal./mole	Heat Capacity cal./deg./mole
273.16. . . .	91.97	0	31.52
300	94.98	862	32.74
500	113.23	8052	38.32
800	132.02	20080	41.31
1000	141.33	28430	42.13
1200	149.06	36910	42.59
1500	158.061	49750	42.98

Hexachloroethane $\text{CCl}_3 \cdot \text{CCl}_3$ (page 2)

Heat Capacity equation for the range 0–1200°C:

$$C_p^\circ = a + b(t) + c(t^2) + d(t^3) \quad (t = ^\circ\text{K})$$

$$a = 31.820; b \times 10^3 = 3.6396; c \times 10^5 = 4.2031; d \times 10^8 = 1.6198$$

Decomposition Temperature: For DTA and TGA see Ref. 38

Decomposition Products: Heated in a stream of air at about 550–600°C it is completely converted to C_2Cl_4 and CCl_4 . 50

Vapor Pressure:

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	31.7	73.5	102.3	124.2	168.8	185.6	186.6

X-Ray Crystallographic Data:

System	Space Group	a	b	c	Molecules/Unit Cell
rhomb.	V_h^{18}	11.51	10.14	6.39	4
cubic		7.43			2

Hygroscopicity:

Solubility Data: In water: insoluble
In benzene, chloroform, oils: soluble
In alcohol and ether: very soluble 1, 29

Health Hazard: May be moderately irritating to the skin and mucous membranes. In high concentrations it has a narcotic effect, and may damage the liver and kidneys. MLD, i.v. (in dogs) 325 mg./kg. Has an odor similar to that of camphor. Moderately toxic locally, on ingestion, and inhalation. 12, 29, 93

Safety Classifications:

OSM: Substantially inert and presents no particular fire or toxic hazard as used in Ordnance establishments.

Fire and Explosion Hazards: Relatively inert, but when heated to decomposition it emits highly toxic fumes of chlorides. Dehalogenation by heating with alkalis and metals, produces explosive chloracetylenes. 12

Nonflammable 53V1

Electrostatic Sensitivity:

Heat of Combustion, Kcal./mole at 20°C and 1 atm.: 110.0

Triple Point, °C:

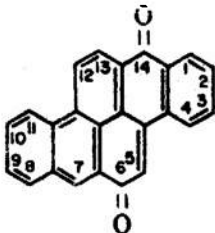
186.0

Use in Pyrotechnics:

as a chlorine carrier
for screening smoke
compositions 1
50V3, 54V3

Additional References:

- 1) E. H. Wibenga, Zeit. anorg. Chem. 225, 38 (1935)
- 2) K. J. Ivin and F. S. Dainton, Trans. Faraday Soc. 43, 32 (1947)
- 3) "Thermodata for Petroleum Chemicals," K. A. Kobe and R. H. Harrison, Petrol. Refiner 36, 155 (1957)

INDANTHRENE GOLDEN YELLOW G.K. (spec. name) (HVT Golden Yellow ; Indanthrene Golden Yellow GKAC; dibenzo(a,h)pyrene-7,14-dione ; 3,4,8,9-dibenzopyrene-7,14-dione; listed in the Ring Index as No. 3654, C.I. 59100, C.I. Vat Yellow 4)		<i>Refs</i>
Structural Formula :	$C_{24}H_{12}O_2$	84
		
Specification No. :	MILD-50029	
Molecular Weight :	332.3	
Crystalline Form :	—	
Color :	golden yellow	88V7 II
Melting Point:	658°K (385°C)	88V7 II
Solubility Data: In dilute NaOH, H ₂ SO ₄ , quinoline, nitrobenzene, xylene,		88V7 11,
tetrahydronaphthalene :	soluble	48A
In acetone, benzene, chloroform, pyridine, toluene :	slightly soluble	
Health Hazard : ~~Some~~ toxicity as indicated by the spec. requirement that "Each container shall be conspicuously labeled : CAUTION—Avoid skin contact ; use with adequate ventilation!"		
Use in Pyrotechnics:	to color smoke mixtures yellow	

KEROSENE (Kerosine, Coal Oil, Lamp Oil, Fuel Oil No. 1)		Refs.
Kerosene is a variable mixture of petroleum hydrocarbons, chiefly of the methane series, 10 to 16 atoms of carbon per molecule.		1, 11, 16
Kerosene is the light oily liquid obtained in the fractionation of petroleum. It is the fraction which is obtained by the overhead distillation of crude petroleum in the 174° and 188° range. It contains hydrocarbons in the range $C_{10}H_{22}$ to $C_{16}H_{34}$. Some commercial kerosenes may include distillates up to 325°C and a specific gravity as high as 0.850. In Pennsylvania, kerosene is defined as having a flash point above 114°F, with not over 10% distillable at 175° and not over 45% up to 200°C. A typical analysis of the kerosene from a midcontinent crude includes n-dodecane, 3 alkyl derivatives of benzene, naphthalene, 1- and 2-methyl-5, 6, 7, 8-tetrahydronaphthalene.		12, 16, 29, 53
The fraction obtained by distillation is decolorized by washing with fuming H_2SO_4 , followed by treatment with sodium plumbite solution and sulfur (Doctor sweetening).		29
Specification No.:	W-K-211C	
Normal Color and Form:	pale yellow to white oily liquid	1
Density, g./ml.:	(liquid) at 60°F, 0.819	1
Coefficient of Thermal Expansion :	—	
Melting Point, °F:	-76	14
Boiling Point, °F:	410-572	14
Decomposition Temperature :	—	
Decomposition Products :	—	
Solubility Data: In water :	insoluble	
With other petroleum solvents :	miscible	29
Health Hazard : Toxic when ingested or inhaled ; causes local irritation, drowsiness, collapse and coma, and may damage the heart, liver, and kidneys.		12, 29
Safety Classifications :		
Underwriters Laboratory Classification :	40	12
OSM :	flammable liquid	
ICC :	not listed	
U.N. :	inflammable liquid	
The ICC does not classify kerosene as a flammable liquid because the flash point is above the maximum for this classification.		

Kerosene (page 2)

Fire and Explosion Hazard: Ignites when exposed to heat or flame. Can also explode in air. To fight fire use foam, CO ₂ , dry chemical, CCl ₄ .	14
Flash point: 100-165°F	75
Autoignition temperature: 490°F	
295°C	71
Explosive limits (% by vol. in air) : 1.16-6.0	26, 75
Explosive limits in closed vessel : 0.7-5	
M.A.C. , parts per million in air for an 8-hr. day : 500	14
Heat of Combustion (for kerosene with sp. gr. 0.819)	
cal./g. : 11,006	71
Use in Pyrotechnics: To prevent dusting in Green Smoke composition I and in Violet Smoke composition II. See specifications MIL-STD-516 and 622.	

LACTOSE, $C_{12}H_{22}O_{11} \cdot H_2O$ (monohydrate)

(Milk Sugar, Sugar of Milk, Lactobiose,

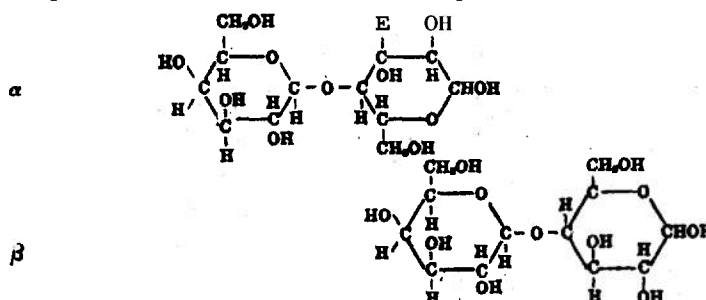
D-Glucose 4-(β -D-galactoside),

D-Glucose 4-(β -D-galactopuranside),

Δ (β -D-galactosyl)-D-glucose,

4-(β -D-galactopyranosyl)-D-glucose)

Chemical Structure: Lactose consists of a glucose unit linked to a galactose unit. Because the glucose unit may be in the form of a lactol ring, α and β forms are possible. The two forms can be represented as follows:



The second formula differs from the first only in that the second glucose ring has been turned through an angle of 180° . The glucoserings may also have the aldehyde structure. Both forms show mutarotation $[\alpha]_D^{20} = +62.3$.

The usual form is the α . By crystallizing solutions of the α form above $93.5^\circ C$, the β form is obtained.

Specification No.:	MILL13751
Molecular Weight:	360.31
Crystalline Form:	rhombic
Color:	colorless
Density, g./ml.:	1.525.
Coefficient of Thermal Expansion:	—
Heat of Formation, cal./mole at $298^\circ K$:	
α -lactose $\cdot H_2O$	-592,900
β -lactose	-583,800
Free Energy of Formation, cal./mole at $298^\circ K$:	
α -lactose $\cdot H_2O$	418,200
β -lactose	-373,700
Entropy, cal./deg./mole at $298^\circ K$:	
α -lactose $\cdot H_2O$	99.1
β -lactose	92.3

Melting Point: $274.7^\circ K$ ($201.6^\circ C$) for the anhydrous material when rapidly heated. The monohydrate when heated loses water and becomes anhydrous at $120^\circ C$.

Refs.

Addnl. Ref. 1

1

1

1

Addnl. Ref. 2

Addnl. Ref. 2

Addnl. Ref. 2

1, 29

Lactose (page 2)

Heat of Fusion:

Boiling Point:

decomposes

Transition Point:

366.6°K (93.5°C)

Addnl. Ref. 3

Heat of Transition, cal./g.:

 α -anhydride to β , + 1.0

Addnl. Ref. 3

Heat of Combustion, anhydrous, Kg.cal./mole (H₂O liquid) at 20° and 1 atm.:

1350.8

1

T, °K	C _p , cal. K°	T, °K	C _p , cal. K°	T, °K	C _p , cal. K°
61.33	21.98			239.02	85.49
65.15	23.63			246.02	87.94
69.70	25.49			252.92	90.65
75.00	27.71			257.99	92.06
81.74	30.37			261.72	93.30
86.85	32.48			268.21	96.65
91.73	34.64			274.33	97.14
96.55	36.12			279.56	99.26
103.74	38.63			284.21	100.74
109.42	40.61			289.17	102.57
115.57	42.97			292.91	103.59
122.23	45.58			293.35	104.10
129.51	48.12			297.42	105.06
140.75	52.11				
	(wt		3.11 g.)		
65.51	22.14	138.72	47.70	217.62	73.62
72.89	25.03	149.22	50.86	225.97	75.81
78.88	27.29	157.75	53.80	235.29	78.62
87.84	30.58	164.86	56.28	243.97	81.35
95.54	33.19	173.35	58.90	252.86	84.53
104.51	36.22	183.05	61.23	262.76	86.95
114.32	39.58	190.47	63.68	270.93	89.60
121.77	42.02	201.24	67.43	280.11	92.89
129.98	44.61	208.73	69.97	289.44	95.55

Decomposition Temperature:

Decomposition Products:

Vapor Pressure:

decomposes

X-Ray Crystallographic Data:

monoclinic system

Lactose (page 3)

Hygroscopicity :

Equilibrium Relative Humidity, % at 25°C : 98.3

Addnl. Ref. 5

Solubility Data: In cold water:

17 g./100 ml. :

In hot water:

40 g./100 ml. :

1

In alcohol:

very slightly soluble

In chloroform and ether:

insoluble

SOLUBILITY IN WATER

Addnl. Ref. 4

Temp. °C	Initial Solubility		Final Solubility	Super Solubility
	α	β		
0	5.0	45.1	11.9	25
25	12.6	—	21.6	50
39	—	—	31.5	74
74	34.4	—	86.2	
89	55.7	—	139.2	
100	—	94.7	—	

Health Hazard:

nontoxic

used in infant feeding

29, 93

Safety Classifications:

OSM:

not listed

ICC:

not listed

Fire and Explosion Hazard (dust ignited electrically in the presence of air) :

86

Concn. mg./l.	Max. Press. lbs./sq. in.	Ave. Rate of Press. Rise lbs./sq. in./sec.	Max. Rate of Press. Rise lbs./sq. in./sec.
100	12	89	177
500	22	32	168

Electrostatic Sensitivity :

—

Apparent Dissociation Constants :

First constant, literature values :

 $0.76-1.05 \times 10^{-12}$

Second constant, literature values :

 $3.0-3.6 \times 10^{-14}$

Third constant:

 1.7×10^{-14}

Fourth constant:

 1.6×10^{-14}

Use in Pyrotechnics :

fuel, retardant, and in
smoke mixtures

Addnl. Ref. 4

Lactose (page 4)

Additional References :

- 1) "Organic Chemistry," G. Hill and L. Kelley, The Blakiston Company, Philadelphia, Pa. (1943)
- 2) "Heat Capacities of Three Disaccharides," A. Anderson and G. Stegman, J. Am. Chem. Soc. 63,2119 (1941)
- 3) J. Am. Chem. Soc. 30, 960-967 (1908)
- 4) "Lactose and Its Utilization, A Review," E. O. Whittier, J. Dairy Science, 27, 505 (1944)
- 5) C.A. 51,17346 (1967)

LAMINAC 4116

Refs.

Laminac 4116, a proprietary product manufactured by American Cyanamid Co., is a polyester with monomeric styrene that effects cross linking on curing. It is used as a bonding agent and for this purpose it is treated with a catalyst to effect curing.

The following data are from the technical data sheet on Laminac Polyester Resins of the Plastics and Resins Division of American Cyanamid Co.

Color:	clear, light straw
Specific Gravity at 77°F:	1.10 ± 0.02
Viscosity at 77°F:	
Gardner Holdt scale	M-0
Brookfield, poises	4-5
(Brookfield Model RVE, spindle #1, 20 R.P.M.)	

Curing Characteristics:

Gel time at 80°C, 100 g. sample, 0.5% benzoyl peroxide, min.:	17-20
SPY gel time, min.:	4½-6
SPI time to peak temp., min.:	7½-9
SPI peak exotherm, °F:	330-360
(SPI = Society of Plastic Industries Test Method)	

The curing of Laminac 4116 is greatly speeded by adding curing agents. The curing is done either at room temperature or by heating. Room temperature curing agents are methylethylketone peroxide and cobalt naphthenate, or benzoyl peroxide and Laminac Promoter 400.

GEE TIMES AT 77°F (Methylethylketone peroxide (60% solution) as the catalyst)

% catalyst	% Cobalt Naphthenate 6% Cobalt metal	Gel time (minutes)
0.5	0.0	200-220
0.5	0.2	130-150
1.0	0.1	50-70
2.0	0.0	40-50
2.0	0.2	10-15

GEL TIMES AT 77°F (Benzoyl peroxide (50% paste) as the catalyst)

% catalyst	% Cobalt Naphthenate 6% Cobalt metal	Gel time (minutes)
1.0	1.0	120-180
2.0	2.0	50-70
4.0	4.0	5-10

Laminac 4116 (page 2)

Heat Curs: Because of the low reactivity of Laminac 4116, its cure may not be complete with **room** temperature catalysts, and heat may be required to complete the cure. Benzoyl peroxide alone may be **used** to cure 4116 at elevated temperatures. Using **0.5-1.0%**, cure **cycles** may be less than 1 minute at 250°F for a section 1/16 in. thick to 10-12 minutes for thicker sections at 200°F.

Safety Classifications :

OSM :

class 2

ICC:

flammable liquid **red** label**Decomposition Temperature :**

about 200°C

For TGA see Addnl. Ref. 5

Decomposition Products :

Hygroscopicity (gain in mg./g. after exposure, at R.T. in static and vacuum desiccators):

Laminac 4116 Catalyzed with Lupersol DDM and Nuodex:

32

Time (days)	65% R.H.		75% R.H.		86% R.H.		93% R.H.	
	Stat.	Vac.	Stat.	Vac.	Stat.	Vac.	Stat.	Vac.
1	3.0	1.5	5.2	3.5	6.6	<1	8.5	3.0
7	5.0	2.5	3.7	4.0	4.7		7.2	2.6
30			0.8		1.0	2.0	1.6	

Storage life of Laminac Resins with and without Catalyst and Accelerator:

Addnl. Ref. 1

Temp. °C	Uncatalyzed (minimum)	With cobalt, but uncatalyzed (minimum)	With 0.004% cobalt and 0.5% Lupersol DDM
	days	days	hours
25	90	90	3.6-4.0
52	18-21	18-21	

As manufactured, Laminac resin contains **0.04%** cobalt, 'as metal.

Additional References:

- 1) "Casting with Laminac Resins," Plastics and Resins Div., American Cyanamid Co., Wallingford, Conn., cited by Ref. 73
- 2) For exotherm cures of Eaminac 4116 with varying amounts of Lupersol DDM and cobalt see Ref. 73
- 3) "The Kinetics of Thermal Degradation of the Synthetic Styrenated Polyester, Laminac 4116," D. Anderson and E. Freeman, J. Appl. Polymer Sc. & 192 (1959)
- 4) "Characterization of Saturated Polyesters by Differential Thermal Analysis," D. Anderson and E. Freeman, Anal. Chem. **31**, 1697 (1959)
- 5) "Pre-ignition and Ignition Reactions of the Propagatively Reacting System Magnesium-Sodium Nitrate-Laminac," V. Hogan and S. Gordon, Combustion and Flame **3**, No. 1, 3-12 (1959)

LEAD CHROMATE, PbCrO_4						Refs.
(Pale Chrome, Permanent Yellow, and Paris, Leipzig, King's, Cologne, or Lemon Yellow Chrome)						1, 11, 12, 29
Percent Oxygen:				19.80		
Specification No.:				JAN-E-488		
Molecular Weight:				323.22		1
Crystalline Form:				monoclinic		1
Color:				yellow or orange-yellow powder		
See also Ref. 54V11						1
Density, g./ml.:				(solid) 6.3		1
Coefficient of Thermal Expansion:				—		
Heat of Formation, Kcal./mole at 298°K:				(c) -217.7		9
Free Energy of Formation, Kcal./mole at 298°K:				-203.6		86
Entropy, cal./deg./mole at 298°K:				36.5		86
Melting Point:				1117°K (844°C)		1
Heat of Fusion:				not available		7
Boiling Point:				decomposes above its melting point and gives off oxygen		1, 54V11
Transition Point, °K:				(c) III $\xrightarrow{980}$ (c) II $\xrightarrow{1056}$ (c) I		9
Heat of Sublimation:				—		
Heat Content or Enthalpy:				—		
Heat Capacity, cal./deg./mole (between 292 and 323°K):				(est.) (solid.) 29.1		4
Decomposition Temperature, °C:				approx. 904		45
For DTA see Ref. 33						
Decomposition Products:				Becomes reddish-brown at 250°C. At high temperatures it fuses and finally evolves oxygen with the formation of Cr_2O_3 and basic lead chromate.		52V3
Vapor Pressure:				—		
X-Ray Crystallographic Data:						
System	Space Group	a	b	c	Axial Angle	Molecules/Unit Cell
monoclinic	C_{2h}^2	6.82	7.48	7.16	$\beta = 102^\circ 33'$	4

Lead Chromate, PbCrO₄ (page 2)

Hygroscopicity (specification **grade material**, after **216 hrs. at 90°F**) :

R.H., %	50	70	90
Gain, %	0.01	0.02	0.09

33

Solubility **Data:** In water at 25°C: **.0000058**

1, 29

In acids and alkali hydroxides: soluble

In acetic acid, ammonia: insoluble

In hot water: insoluble

Health Hazard: ~~Partakes~~ of the poisonous nature of **both lead and chromium salts**, Corrosive action on the skin, produces ulcers, and is **associated with** the formation of **cancers**. Produces anemia. Because of its low solubility, its toxicity is less than ~~most~~ other lead **salts**.

12

M.A.C., mg./m.³ 0.1

14

Safety Classifications:

OSM : Class **2**, when not packed or stored in original shipping container.

Fire and Explosion Hazard: ~~Moderate~~ by **chemical** reaction with ~~reducing~~ agents. Dangerous when ~~heated~~, as it ~~emits~~ highly **toxic** fumes of lead.

12

Electrostatic Sensitivity :

Use in Pyrotechnics: ~~As~~ an oxidizing **agent**. ~~Used~~ in nongaseous powders.

LEAD OXIDE, PbO			Refs.
(Litharge, Massicot, Plumbous Oxide, Lead Protoxide, Lead Monoxide, Lead Oxide Yellow)			1, 29
Massicot refers to the unfused oxide and litharge, to the fused. Modern usage tends to the use of litharge for all varieties of PbO.			
Specification No. (litharge, dry) :	MIL-L-1147A		
Molecular Weight :	223.21		
Crystalline Form (litharge) :	tetragonal—stable at R.T.		
(massicot) :	rhombic—stable, 300°C to M.P.	22	
Color :	yellow		
For the effect of temp. See Ref. 52V7			
Density, g./ml.:	(solid) α litharge, 9.53 β massicot, 8.0	1	
Coefficient of Thermal Expansion, cubic :	7.95×10^{-5}	54V7	
Heat of Formation, Kcal./mole, at 298°K :	red (c) -52.40 yellow (c) -62.07	8, 9	
See Tables a, b, c			
Free Energy of Formation, Kcal./mole at 298°K :	red (c) -45.25 yellow (c) -46.05	1, 8, 9	
See Tables a, b, c, and equations			
a. HEAT AND FREE ENERGY OF FORMATION OF PbO (red, yellow)			2 ,
T, °K	ΔH (cal./mole)	ΔF° (cal./mole)	
298.16	-52,450 ($\pm$ 400)	-45,250 ($\pm$ 150)	
400	-52,250	-42,850	
500	-52,050	-40,500	
600	41,800	-38,200	
600.5	-51,800	-38,200	
600.5	-53,050	-38,200	
700	-52,800	35,750	
762	-52,600	-34,250	
762	-52,350	34,250	
Phase Changes of Metal			
M.P., 600.5°K ; $\Delta H = 1225$ cal./g.-atom			

Lead Oxide, PbO (page 2)

b. HEAT AND FREE ENERGY OF FORMATION OF PbO (yellow, 1, g)

2

T, °K	ΔH (cal./mole)	ΔF° (cal./mole)
298.16	-52,050 (± 300)	-45,050 (± 150)
400	-51,900	-42,700
500	-51,750	-40,400
600	-51,550	-38,150
600.5	41,550	-38,150
600.5	-52,800	-38,150
700	-52,500	-35,750
800	-52,200	-33,350
900	-51,850	-31,000
1000	-51,460	-28,760
1100	51,000	-26,460
1159	-50,700	-25,150
1159	-47,900	-25,150
1200	-47,700	-24,409
1300	-47,250	-22,450
1400	-46,750	-20,550
1500	-46,250	-18,700
1600	-45,750	-16,850
1700	-45,800	-16,100
1745	45,100	-14,300
1745	+5,700	-14,300

Phase Changes of Metal
M.P., 600.5°K; $\Delta H = 1226$ cal./g.-atom

c. HEAT AND FREE ENERGY OF FORMATION OF PbO(g)

2

T, °K	ΔH (cal./mole)	ΔF° (cal./mole)
298.16	+10,100 (± 1400)	+5000 (± 1500)
400	+9900	+3200
500	+9700	+1600
600	+9500	0
600.5	+9500	0
600.5	+8300	0
700	+8000	-1400
800	+7800	-2700
900	+7600	-4000
1000	+7400	-5300
1100	+7200	-6600
9200	+7000	-7800
1300	+6700	-9000
1400	+6500	-10,300
1500	+6300	-11,400
1600	+6000	-12,600
1700	+5800	-13,800
1800	+5600	-15,000
1900	+5300	-16,100
2000	+5100	-17,200

Phase Changes of Metal
M.P., 600.5°K; $\Delta H = 1225$ cal./g.-atom

Source of Data : Heat of formation at 1745°K derived from heat of formation and heat of vaporization of PbO (1) (see. Table b)

Pb
=

Pb

=

2

2
3

2, 9

2, 9

2, 8, 9

9

9

2

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	1150	3.32	1100	10,800	16.90
500	2340	5.97	1159 (c) . . .	11,720	17.72
600	3600	8.26	1159 (l) . . .	18,720	23.76
700	4920	10.30	1200	19,380	24.32
800	6310	12.15	1300	20,980	25.60
900	7760	13.86	1400	22,580	26.79
1000	9260	15.44	1500	24,180	27.89

Lead Oxide, PbO (page 4)

e. HEAT CONTENT AND ENTROPY OF PbO (red)
(Base, crystals at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	1220	3.52	700	5060	10.65
500	2460	6.28	800	6420	12.46
600	3740	8.62	900	7820	14.11

Enthalpy : $H_T - H_{298.15} = 10.60T + 2.00 \times 10^{-5}T^2 - 3338$ (0.1 percent; 298–900°K)

Heat Capacity: $C_p = 10.60 + 4.00 \times 10^{-5}T$

f. HEAT CONTENT AND ENTROPY OF PbO (g)
(Base, crystals at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	810	2.34	1000	5950	10.14

PbO (g) :

Enthalpy : $H_T - H_{298.15} = 8.57T + 0.12 \times 10^{-5}T^2 + 0.79 \times 10^5T^{-1} - 2831$
(0.2percent ;298–2000°K)

Heat Capacity : $C_p = 8.57 + 0.24 \times 10^{-5}T - 0.79 \times 10^5T^{-2}$

PbO (c) :

Heat Capacity : $C_p = 12.70 + 7.80 \times 10^{-5}T$ (est.) (298–1000°K)

Pb₃O₄ (c) :

Heat Capacity : $C_p = 35.14$ (298°K)

Pb₂O₃ (c) :

Heat Capacity : $C_p = 25.74$ (298°K)

See also Addnl. Ref. 2

Heat Capacity, cal./deg./mole at 298°K : (solid, yellow) 11.60
(liquid) 16.00

4, 9

See also Addnl. Ref. 2

Decomposition Temperature and Products : At 300–450°C, in air, it is converted to Pb₃O₄, but at higher temperatures it is reconverted to PbO.

29, Addnl.
Ref. 1,
54V7

For DTA see Ref. 33

Lead Oxide, PbO (page 5)

Vapor Pressure :

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	943	1086	1189	1265	1402	1472	890

X-Ray Crystallographic Data :

System	Space Group	a	b	c	Molecules/Unit Cell
tetragonal (red)	D _{4h} ⁷	3.98	—	4.01	2
rhombic (yellow)	V _P ⁹	5.60	4.72	5.88	4

R.H.%	31	43	65	75	93
Time of Exposure	24 hrs. equil.	24 hrs. equil.	24 hrs. equil.	24 hrs. equil.	24 hrs. equil.
Gain mg./g.	1.3 2.6	1.2 3.9	4.7 3.8	5.1 6.6	7.4 7.5

Solubility Data: In water:

.0017 g./100 g at 20°

In **HNO₃**, alk. lead acetate, **NH₄Cl**, **CaCl₂**, **SrCl₂**, and warm solutions of fixed alkali hydroxides:

soluble

In alcohol:

insoluble

Health Hazard: More poisonous than metallic lead or most other lead compounds. Avoid breathing dust. Wear approved dust mask, ~~Keep~~ away from food or food products:

M.A.C., mg./m.³:

0.2

0.15

Safety Classifications:

OSM:

not listed

ICC:

no shipping label required

Fire and Explosion Hazard : Dangerous. When heated emits highly toxic fumes.

Electrostatic Sensitivity :

—

Use in Pyrotechnics:

—

Additional References :

1) C.A. 52,6998 (1958)

2) "Low Temperature Heat Capacities and Entropies at 298.15°K of Lead Sesquioxide and Red and Yellow Lead Monoxide," E. G. King. J. Am. Chem. Soc. 80,2400 (1958)

LEAD OXIDE (LEAD TETROXIDE). Pb_3O_4
 (Minium, Red Lead, Mineral Orange, Mineral Red,
 Plumbo, Puce, Orthoplumbate, Paris or Saturn Red)

Refs.
 1, 11, 29

Type II paste in oil, grade 97.

Molecular Weight: **685.63**
 Crystalline Form: **scales or amorphous powder**
 Color: **red**

1
 1
 54V7

When heated becomes redder, then violet and black; on cooling again regains its scarletred color.
 Density, g./ml.: (solid) **9.1**

1
 54V

Varies from 8.32 to 9.16 according to method of preparation.

Coefficient of Thermal Expansion: —

Heat of Formation, Kcal./mole at 298°K: -175.6

1, 8,

See table below

Free Energy of Formation, Kcal./mole at 298°K: -147.8

1, 8,

See table below

HEAT AND FREE ENERGY OF FORMATION OF Pb_3O_4 (c)

T, °K	ΔH (cal./mole)	ΔF° (cal./mole)
298.16	-175,500 (± 4000)	-147,500 (± 4600)
400	-175,500	-138,000
500	-175,000	-129,000
600	-174,500	-119,500
600.5	-174,500	-119,500
600.5	-178,000	-119,500
700	-177,500	-110,000
800	-176,500	-100,500
900	-175,000	-91,000
1000	-173,500	-81,500

Phase Changes of Metal

M.P., 600.5°K; $\Delta H = 1225$ cal./g.-atom

Free Energy Equations:

2

Reaction	Range of Validity, °K
1) $3Pb(c) + 2O_2(g) = Pb_3O_4(c)$ $\Delta F_T = -174,920 + 8.82T \log T - 8.20(10^{-3}T^2) - .40(10^5T^{-1}) + 72.78T$	298.16-600.5
2) $3Pb(l) + 2O_2(g) = Pb_3O_4(c)$ $\Delta F_T = -177,860 + 15.59T \log T - 11.05(10^{-3}T^2) - .40(10^5T^{-1}) + 60.57T$	600.5-1000
Entropy, cal./deg. mole at 298°K:	50.5

3, 9, 24

Lead Oxide, Pb₃O₄ (page 2)

Melting Point:

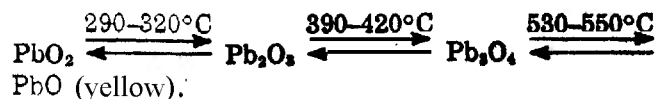
decomposes at about
773°K (500°C)

See Decomposition Temperature

Heat of Fusion:

Boiling Point:

Transition Point:



Heat of Sublimation:

Heat Content or Enthalpy:

Heat Capacity, cal./deg./mole at 298°K: (solid) 35.14

Decomposition Temperature and Products. Heated in air above 450°C, it is converted to PbO. About 550°.

Stable at 530°C.

For TCA see Kef. 45

Vapor Pressure:

	for Pb ₃ O ₄ $\xrightleftharpoons{+1/2 \text{ O}_2}$ PbO (yellow)						
Press. mm.	8.4	3.04	76.0	155	589	859	1045
Temp. °C	444.8	484.4	511.2	537.6	558.3	600.7	607
or $\log_{10} p_{\text{mm.}} = -7.8595T^{-1} + 11.8976$							

X-Ray Crystallographic Data:

System	Space Group	a	c	Molecules/Unit Cell
tetragonal	V ₄	8.875	6.51	4

Hygroscopicity (of reagent grade material after equilibrium was established in a vacuum desiccator):

R.H.%	65	75	86	93
Time of Exposure	24 hrs. equil.	24 hrs. equil.	24 hrs. equil.	24 hrs. equil.
Grin. mg./g.	0.5 0.9*	0.2 0.1*	0.4 0.4*	0.8 0.6'

Solubility Data: In water and alcohol:

In acetic acid, hot HCl

insoluble
soluble

Health Hazard: A cumulative poison that produces anemia and lesions of the kidneys, liver, nervous system, blood vessels, and other tissues. The specification requires the following warning label: "Warning! Contains Lead Oxide Hazardous Dust. Avoid breathing dust and fumes. After handling or exposure do not eat or smoke without washing thoroughly. Use with adequate ventilation. Keep away from food or food products."

M.A.C., mg./m.³:0.2
0.15

Lead Oxide, Pb_2O_3 (page 3)

Safety Classifications :

OSM :

ICC :

class 2

oxidizing material

yellow label

Fire and Explosion Hazard: Dangerous because when it is heated it emits highly toxic fumes. It reacts with combustible and reducing agents. 12

Electrostatic Sensitivity:

Use in Pyrotechnics:

as an oxidizer

17

Additional References :

- 1) C.A. 52, 6998 (1968)

LEAD PEROXIDE, PbO_2			Refs.
(Lead Dioxide, Lead Superoxide, Brown ¹ Lead Oxide, Plattnerite)			1, 12, 29
Percent Oxygen:	18.38		
Specification No.:	JAN-L-376		
Molecular Weight:	239.21		
Crystalline Form:	tetragonal		1
Color:	brown		
Density, g./ml.:	(solid) 9.876 (reguline at 20°C) 9.86		Addnl. Ref. 3
Coefficient of Thermal Expansion, linear:	0.067×10^{-4}		54V7
Heat of Formation, Kcal./mole at 298°K:	(c) -66.12		1, 9
See table below			
Free Energy of Formation, Kcal./mole at 298°K:	-62.34		1, 9
See table below			
HEAT AND FREE ENERGY OF FORMATION OF $\text{PbO}_2(\text{c})$			2
T, °K	ΔH (cal./mole)	ΔF° (cal./mole)	
298.16	-66,100 (± 1400)	-52,300 (± 1200)	
400	-65,900	-47,700	
500	-65,700	-43,100	
600	-65,500	-38,600	
600.5	-65,500	-38,600	
600.5	-66,700	-38,600	
700	-66,400		
800	—	-29,400	
900	-65,500	-24,800	
1000	-65,000	-20,300	
1100	-64,400	-15,900	
Phase Changes of Metal			
M.P., 600.5°K $\Delta H = 1225 \text{ cal./g.-atom}$			
Entropy, cal./deg./mole at 298°K:	18.3 $\pm$ 0.5		3, 9
Melting Point:	decomposes		1
Heat of Fusion:	—		
Boiling Point:	—		
Transition Point: See Lead Oxide (Lead Tetroxide), Pb_2O_4			
Heat of Sublimation:	—		
Heat Content or Enthalpy:	—		
Heat Capacity, cal./deg./mole at 298°K:	(solid) 15.4		9
Decomposition Temperature, °C:	290		1

Lead Peroxide, PbO₂ (page 2)

Decomposition Products : Evolves **oxygen** when heated above 300°C, first forming Pb₃O₄, and at high temperatures PbO.

17V8, 29
Addnl.
Ref. 5

54V7
1

32

R.H., %	65		76		86		93	
Time of Exposure	24 hrs.	equil.	24 hrs.	equil.	24 hrs.	equil.	24 hrs.	equil.
Gain, mg./g.	0.3 0.1	0.2* 0.2	0.2 0.4	0.2* 0.6	0.1 0.8	.03	0.8 0.3	0.9 0.0

Solubility : In water and alcohol :

insoluble

In dil. HCl :

soluble

In acetic acid :

slightly soluble

Health Hazard: A cumulative poison. On ingestion or **inhalation** it produces anemia of the kidneys, liver, gonads, nervous system, blood vessels, and other tissues.

1

12, 17V8

M.A.C., mg./m.³ :

0.2

25

0.15

14

Safety Classifications:

OSM : Class 2 when not packed or stored in original containers or equivalent
ICC: oxidizing material;
yellow label

Fire and Explosion Hazard : Dangerous **because** when heated to decomposition it emits highly toxic **fumes** of lead. It reacts with **reducing** material.

12

Electrostatic Sensitivity :

Changes under Heat and Oxygen Pressure : Under 200 atmospheres of oxygen PbO₂ is unstable to 360-365°C, but then dissociates to form Pb₇O₁₁ which is stable to 460-470°C when it passes into Pb₃O₄.

Addnl. Ref. 4 .

Use in Pyrotechnics:

as an oxidizer

17

Additional References :

- 1) "The Thermal Decomposition of Lead Dioxide in Air," G. Butler and J. Copp, J. Chem. Soc., **725 (1956)**
- 2) "Structure and Equilibria of Lead Oxides." See C.A. **43,6689 (1948)**
- 3) "The Electrical Conductivity and Some Other Properties of Reguline Lead Peroxide," W. Palmaer, Z. Elektrochem **29, 415 (1923)** ; C.A. **18 616 (1924)**
- 4) "A New Oxide of Lead," C. Holtermann and P. Lafitte, Compt. rend. **204, 813 (1927)** ; C.A. **31, 5702 (1937)**
- 5) C.A. **52,6998 (1958)**

LEAD SESQUIOXIDE						Refs.
(Lead (III) Oxide, Lead (II, N) Oxide, Lead Trioxide Plumbous Plumbate, Di-lead Trioxide)						1, 50
Formula :		Pb₂O₃				52V7
Pb ₂ O ₃ is generally considered to be lead metaplumbate (PbO·PbO ₂) or a compound of PbO and PbO ₂ into which it is decomposed by acids.						
Percent Oxygen :		10.38				
Specification No. :		none				
Molecular Weight :		462.42				
Crystalline Form :		monoclinic or amorphous , .powder				1
Color:		yellow to reddish-yellow				1
Density :		—				
Coefficient of Thermal Expansion :		—				
Heat of Formation :		—				
Free Energy of Formation :		—				
Entropy, cal./deg./mole at 298.15°K :		36.3 ± 0.7				Addnl. Ref. 1
Melting Point:		decomposes about 643°K (370°C)				1
Heat of Fusion:		—				
Boiling Point :		—				
Transition Point :		see Lead Oxide (Pb ₂ O ₄)				
Heat of Sublimation :		—				
Heat Content or Enthalpy:		—				
Heat Capacity, cal./deg./mole at 298°K :		(solid) 26.74				4, Addnl. Ref. 1
Decomposition Temperature: At 360–415°C, it forms red lead with loss of O						54V7
At red heat yields PbO + O.						
Decomposition Products : Converted in air at 370°C to Pb ₂ O ₄ .						29
Vapor Pressure :		—				
X-Ray Crystallographic Data :						18
System	Space Group	a	b	c	Axial Angle β = 80°6'	Molecules/ Unit Cell
monoclinic	C _{2h} ²	7.050	5.616	3.866		2
Hygroscopicity :		—				
Solubility Data: Insoluble in cold water, decomposes in hot. Decomposed by conc. HCl or H ₂ SO ₄ with the liberation of Cl or O respectively.						1 29

Lead Sesquioxide (page 2)

Health Hazard: A cumulative poison when ingested, inhaled, or absorbed.

M.A.C., mg./m.³ :

0.2

12

25

Safety Classifications:

OSM: Not listed. Probably class 2 when not packed or stored in original shipping container or equivalent.

ICC :

not listed

Fire and Explosion Hazard:

—

Electrostatic Sensitivity:

—

Use in Pyrotechnics:

as an oxidizing agent

Additional References :

- 1) "Low Temperature Heat Capacities and Entropies at 298.15°K of Lead Sesquioxide and Red and Yellow Lead Monoxide," E. G. King, J. Am. Chem. Soc. 80, 2400 (1958)

LINSEED OIL

(Bung Oil, Bung Hole Oil, Linum Usitatissimum)

Refs.

Linseed oil is obtained by pressing the seeds of the flax plant. The commercial oil is hot pressed. When fresh, the oil is yellowish with a peculiar odor and a bland taste; however, the hot pressed oil has a bitter taste. On exposure to the air, the oil slowly oxidizes, becoming darker, more viscous and acquires a stronger taste and odor. Boiled linseed oil is prepared by heating with metallic oxides, usually of lead or manganese (called driers). Such oil is called bung oil or bung hole oil. The state law of Ohio defines linseed oil as prepared pure linseed oil heated to a temperature of 225°F, incorporating not more than 4% by weight of drier, and with a specific gravity at 60°F of not less than 0.935 and not greater than 0.945. The oil dries in air with a glassy appearance and makes a hard yellowish film. The oxidized elastic solid is known as linoxyn.

16, 29, 57
Addnl. Ref. 3

Linseed oil is a mixture of glycerides of higher fatty acids, both saturated and unsaturated. Of these linoleic acid is about 48% and linolenic acid about 34%. Glycerides of stearic, palmitic, and myristic acids are also present. Addnl. Ref. 3 gives the following fatty acid analysis: 0.2 myristic, 6.4 palmitic, 3.5 stearic, 0.6 arachidic, 9.6 oleic, 42.6 linoleic, 38.1 linolenic.

Specification (for boiled linseed oil) :	TT-O-364	
(for raw linseed oil) :	TT-O-369	
Density, g./ml.:	0.930-0.938	1
Solidification Point, °C:	-19 to -27	1
Boiling Point:	616°K (343°C) 588.7°K (315.6°C) (600°F)	12 67
Decomposition Temperature and Products :	—	
Hygroscopicity:	nonhygroscopic	
Solubility Data:		
In alcohol:	slightly soluble	29
With chloroform, ether, petroleum ether, CS ₂ , and oil of turpentine:	miscible	
Health Hazards: Slight. Boiled linseed oil contains a small amount of manganese dioxide. Because of this, if it is splashed in the eyes, it will cause extreme irritation. When handling keep linseed oil away from fire or open flame. Store it in a sealed container and away from oxidizing agents. If linseed oil has been splashed into the eyes, wash the eyes in a solution of one part vinegar and four parts water by volume. Send the victim to a physician for examination and additional treatment.		12
Safety Classifications:		
OSM: Not classified, but listed as a flammable liquid.		
ICC:	not listed	
Fire and Explosion Hazard: Flammable and can ignite spontaneously. To fight fire use foam, CO ₂ , dry chemical, or CCl ₄ .		26, 67, 75
Electrostatic Sensitivity:	—	

Linseed Oil (page 2)

Constants for Linseed Oil (raw) :

Maumené number :	103-126
Acid value :	1-3.5
Refractive index, N_D^{25} :	1.4797-1.4802
Reichert-Meissl number :	0.95
Unsaponified matter :	0.4-1.2
Saponification value :	188-195
Iodine value :	175-202
Hehner's number :	94.5-95.5

Flash Point (~~closed~~ cup) **CF** (literature references vary) :
(raw) from 432 to 468
(boiled) from 878 to 408

Autoignition Temperature, **°F** :

Literature references give values ranging from 650 to 820.

Use in Pyrotechnics:

as a binder, a retardant
and to reduce
hygroscopicity

Additional References :

- 1) "The Chemical Constitution of Natural Fats," T. P. Hilditch, London (1956)
- 2) "Vegetable Fats and Oils," E. W. Eckey, Reinhold Pub. Corp., New York (1954)
- 3) "Fats and Oils," H. G. Kirschenbauer, Reinhold Publishing Co., New York (1944)

LITHIUM, Li

Refs.

Specification No. :	---	
Molecular Weight:	6.940	
Crystalline Form :	cubic	1
Color :	silvery white, yellows on exposure to moist air	29
Density, g./ml. :	(solid) 0.684	1
Coefficient of Thermal Expansion, linear, 0-95°C :	56×10^{-6}	27
	cubic, 0-178°C : 170×10^{-6}	
Heat of Formation, Kcal./mole at 298°K :	(gas) 37.07	1, 5
Free Energy of Formation, Kcal./mole at 298°K :	(gas) 29.19	1, 5
Entropy, cal./deg./mole at 298°K :	(gas) 33.14	1, A
See Tables a, b, and c		
Melting Point :	726.8°K (453.70°C)	4, 5
Heat of Fusion, cal./mole:	722.8	5
Boiling Point :	1604°K (1331°C)	5
Heat of Vaporization, cal./mole :	32,990	5
'transition Point :	(c) II $\rightarrow$ I 77°K (-196°C)	5, 41'
Heat of Sublimation, cal./mole at 298°K :	(monatomic gas) 38,440	
	(diatomic gas) 50,470	5
Heat Content or Enthalpy, cal./mole at 298°K :	(solid) 1092	
	(diatomic gas) 2312	5
See Tables a, b, and c		
a. HEAT CONTENT AND ENTROPY OF Li (c, l)		4
(Base, crystals at 298.15°K)		

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
350	315	0.97	900	4845	9.08
400	630	1.82	1000	5535	9.80
453.7 (c) . .	1000	2.68	1100	6225	10.46
453.7 (l) . .	9715	4.26	1200	6910	11.06
500	2050	4.96	1300	7595	11.61
600	2765	6.26	1400	8280	12.12
700	3465	7.34	1500	8960	12.53
800	4155	8.27	1600	9645	13.03

Li (c) :

Enthalpy : $H_T - H_{298.15} = 1.64T + 5.55 \times 10^{-5}T^2 - 0.84 \times 10^{-8}T^{-1} - 701$ (0.1 percent; 298-453.7°K)

Heat Capacity: $C_p = 1.64 + 11.10 \times 10^{-5}T + 0.84 \times 10^{-8}T^{-2}$; $\Delta H_{453.7}$ (fusion) = 715

Lithium, Li (page 2)

Li (l) :

Enthalpy: $H_T - H_{298.15} = 6.78T - 0.99 \times 10^{-5}T^2 - 1143$ (0.1 percent; 453.7 - 1800°K)

Heat Capacity: $C_p = 6.78 + 0.99 \times 10^{-5}T^2$

4

b. HEAT CONTENT AND ENTROPY OF Li (g)
(Base, ideal gas at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	505	1.46	1900	7960	9.20
500	1005	2.57	2000	8460	9.46
600	1500	3.48	2200	9460	9.94
700	1995	4.24	2400	10,460	10.37
800	2495	4.90	2600	11,470	10.78
900	2990	5.49	2800	12,496	11.16
1000	3490	6.01	3000	18,626	11.51
1100	3985	6.49	3500	16,190	12.33
1200	4480	6.92	4000	19,010	13.08
1300	4980	7.32	4500	22,030	13.80
1400	5475	7.69	6000	25,316	14.49
1500	6975	8.08	6000	33,070	15.90
1600	6470	8.35	7000	43,240	17.46
1700	6965	8.65	8000	56,610	19.23
1800	7465	8.94			

Li (g) :

Enthalpy: $H_T - H_{298.15} = 4.971T - 1482$ (0.2 percent; 298-3000°K)

c. HEAT CONTENT AND ENTROPY OF Li₂ (g) :
(Base, ideal gas at 298.15°K; mol. wt., 13.88)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
460	890	2.59	1300	9115	13.30
500	1780	4.57	1400	10,060	14.00
600	2675	6.20	1500	10,985	14.64
700	3580	7.61	1600	11,925	15.25
800	4490	8.81	1700	12,865	15.82
900	5410	9.90	1800	13,815	16.36
1000	6330	10.87	1900	14,770	16.88
1100	7250	11.74	2000	15,725	17.37
1200	8180	12.56			

Lithium, Li (page 3)

Li_2 (g) :

Enthalpy: $H_T - H_{298.15} = 8.93T + 0.16 \times 10^{-8}T^2 + 0.36 \times 10^{-5}T^{-1} - 2797$
(0.1 percent; 298-2000°K)

Heat Capacity: $C_p = 8.93 + 0.32 \times 10^{-8}T - 0.36 \times 10^{-5}T^{-2}$

Heat Capacity, cal./deg./mole at 298°K :
(solid) 6.91
(gas, monatomic) 4.97
(gas, diatomic) 8.62

d. HEAT CAPACITY OF Li

Solid	298-453.7°K
Liquid	453.7-1604°K
Gas (mon.)	1604-3000°K
T, °K	C_p° (cal./deg./mole)
298	5.91
400	6.50
500	7.20
600	7.06
900	6.90
1200	6.87
1600	6.80
1700	4.97
2000	4.98
2400	5.03
2800	5.13
3000	5.21

Decomposition Temperature: _____

Decomposition Products: _____

Vapor Pressure:

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	723	881	1003	1097	1273	1372	186

X-Ray Crystallographic Data :

<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>Atoms/Unit Cell</i>
cubic	O_h^2	3.502	2

Hygroscopicity : Reacts with water ; forms LiOH, evolves H_2 .

Solubility Data: In water : forms LiOH, evolves H_2

in alcohol: decomposes

In acids: soluble, reacts and evolves H_2

In liquid NH_3 : soluble

Health Hazard : Will burn in contact with many substances, producing a caustic smoke which is toxic by inhalation. Dangerous when ingested or inhaled, and produces painful burns when in contact with the skin.

Lithium, Li (page 4)

Safety Classifications:

OSM: Not specifically listed; probably class 2 as a powdered metal
ICC: flammable solid, yellow label

Fire and Explosion Hazard: Dangerous explosive hazard when exposed to heat, flame, or by chemical reaction with water, acids or oxidizers. On burning, it emits toxic fumes of Li_2O and LiOH . It burns in air with a dazzling bright light. Keep the metal submerged in kerosene. Store and process only in rooms or buildings adequately vented at the highest point to prevent the accumulation of hydrogen gas which results from the reaction with moisture. Suitable respiratory protective equipment and self-contained breathing apparatus should be used where permissible concentrations are likely to be exceeded. To fight fire, use special mixtures of dry chemicals, soda ash, or graphite.

14, 12, 16

Autoignition Temperature, °F:

392

12

Electrostatic Sensitivity:

—

Use in Pyrotechnics: Burns with a brilliant crimson to carmine-red color.

1, 29

LITHIUM NITRATE, LiNO_3

Refs.

Percent Oxygen :	69.62	
Specification No. :	—	
Molecular Weight :	68.95	
Crystalline Form :	trigonal	1
Color :	colorless	
Density, g./ml. :	(solid) 2.38	1
(liquid) $d = 1.924 - .548 \times 10^{-4} t^\circ\text{C}$ (M.P. to 550°C)		40V2
Coefficient of Thermal Expansion, at 254°C		
(molten) cubic :	about 3.15×10^{-4}	44V20
Heat of Formation, Kcal./mole at 298°K :	(c) -116.28	1, 9
Free Energy of Formation, Kcal./mole at 298.16°K :	-96.63	86
Entropy, cal./deg./mole at 298.16°K :	38.4	86
See table below		
Melting Point :	525°K (252°C)	4
Heat of Fusion, cal./mole :	6120	4
Boiling Point :	decomposes	
Transition Point :	—	
heat of Sublimation :	—	

HEAT CONTENT AND ENTROPY OF LiNO_3 (c, l) (Base, crystals at 298.15°K)

4

$T, ^\circ\text{K}$	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	$T, ^\circ\text{K}$	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
353	1130	3.50	525 (c) . . .	5380	13.29
400	2280	6.57	525 (l) . . .	11,500	24.95
450	3480	9.39	550	12,160	26.18
500	4730	12.03	600	13,490	28.49

LiNO_3 (c) :

Enthalpy: $H_T - H_{298.15} = 14.981 + 10.60 \times 10^{-5} T^2 - 5409$ (0.1 percent; $298-525^\circ\text{K}$)

Heat Capacity: $C_p = 14.98 + 21.20 \times 10^{-5} T$

LiNO_3 (l) :

Enthalpy: $H_T - H_{298.15} = 26.60T - 2470$ (0.1 percent; $525-600^\circ\text{K}$)

Heat Capacity, cal./deg./mole : (liquid) 26.60

Decomposition Temperature and Products : When heated, gives off oxygen then a mixture of oxygen and nitrogen.

For DTA and TGA see Refs. 33, 47

Vapor Pressure: —

4

54V2

Lithium Nitrate, LiNO₃ (page 2)

X-Ray Crystallographic Data :

System	Space Group	a	Axial Angle	Molecules/ Unit Cell	
hexagonal	D _{3d} ⁵	5.74	$\alpha = 48^{\circ}3'$	2	1
Solubility :					
In water (g./100 ml.) :				52 cold, 66 at 71°C	1
In acetic acid :				slightly soluble	
Hygroscopicity : Deliquescent. Caution : Keep in closed containers.					29
Health Hazard : Large amounts taken by mouth may be fatal .					12
Safety Classifications:					
OSM : Class 1 . Class 2 when not packed or stored in original shipping containers or equivalent.					
ICC :				oxidizing material	
Fire and Explosion Hazard: A vigorous oxidizing agent. May explode when heated with a fuel, or when exposed to heat or by shock . On decomposition it emits toxic fumes.					
Electrostatic Sensitivity :					
Use in Pyrotechnics:					17
				as an oxidizer ;to color burning compositions red	

LITHIUM PERCHLORATE, LiClO_4				Refs.
Percent Oxygen:	60.15			
Specification No.:	none			
Molecular Weight:	106.40			
Crystalline Form:	no regular form recognizable			14V20
Color:	colorless			1
Density, g./ml.:	(solid) 2.429			1, 65
coefficient of Thermal Expansion:	—			
Heat of Formation, Kcal./mole at 298°K:	-91.77			72
Free Energy of Formation:	—			
Entropy:	—			
Melting Point:	509°K (236°C) 520°K (247°C)			9 Addnl. Ref. 1
Values vary from < 300 to 410°C, with decomposition.				65
Boiling Point:	decomposes at 653°K (380°C)			1
Transition Point:	—			
Heat of Sublimation:	—			
Heat Content or Enthalpy:	—			
heat Capacity:	—			
Decomposition Temperature, °C:	380			1
For DTA and TGA see Refs. 33, 47				
Decomposition Products:	$\text{LiCl} + \text{O}_2$			29
Decomposition:	Does not begin to show an appreciable decomposition rate until the temperature is raised to over 400°C.			72
There is an endothermic break at 610°C, corresponding closely to the melting point of LiCl (614°C). At about 420°C LiClO_4 begins to undergo appreciable loss. The temperature interval between salt fusion and onset of rapid decomposition is from 247 to about 502°C, or approximately a range of 255°C:				Addnl. Ref. 1
$\text{LiClO}_4 \cdot \text{H}_2\text{O}$ loses H_2O at 146°C				Addnl. Ref. 1
The pure anhydrous salt can be heated to at least 300°C without decomposition, but ordinary samples decompose at lower temperatures to chloride and oxygen owing to the catalytic effect of dust and atmospheric impurities.				52V7
Vapor Pressure:	—			
X-Ray Crystallographic Data for $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$:				1
System	Space Group	a	c	
hexagonal	C_{6v}	7.71	5.42	
Hygroscopicity:	deliquescent			1
Solubility Data: in water (g./100 g.):	59.7 at 25°C			1

Lithium Perchlorate, LiClO₄ (page 2)

Solubility in Nonaqueous Solvents at 25°C

65, 72, 77

<i>Solvent</i>	<i>g./100 g. of Solvent</i>
acetone	136.5
ethyl acetate	95.2
ethyl ether	113.7
methyl alcohol	182
ethyl alcohol	151.8

Health Hazard: May irritate the **skin** and mucous membranes. **Lithium** salts are rated moderately toxic. They affect the nervous systems, and **can** cause death.

29, 65

Safety Classifications :

OSM: **Class** 1. Class 2 when not stored in original shipping containers or equivalent.

ICC: Oxidizing material; yellow label. Classed under "Explosives and Other Dangerous Articles."

Fire and Explosion **Hazard:** A powerful oxidizer, **can** cause fires by chemical reaction, and forms explosive mixtures with carbonaceous materials or finely divided metals, sulphur, powdered magnesium or aluminum. **Explodes** on shock or by chemical reaction.

12

Electrostatic Sensitivity :

Use in Pyrotechnics :

as an oxidizer ; to color
burning compositions red

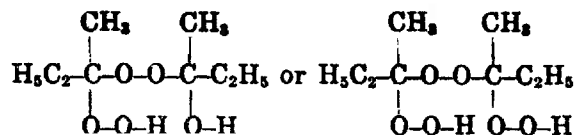
Additional References :

- 1) "The Differential Thermal Analysis of Perchlorates. **11. The System** LiClO₄ - LiCO₃," **M. M.** Markowitz, J. Phys. Chem. **62**, 827 (1968)
- 2) "Precise Studies of the Crystal Structures of Lithium Perchlorate Trihydrate, Anhydrous Lithium Perchlorate, and **Potassium** Perchlorate," R. J. Prosen and K. N. Trueblood, Perchlorates **TN-2, OSR TN 56-563**, ASTIA Document **No. AD110-384** (1956)

LUPERSOL DDM

Lupersol DDM is a proprietary mixture of 60% methylethylketone peroxide in dibutylphthalate, marketed by the Lucidol Div., Wallace and Tiernan, Inc., Buffalo, New York. The following data, except where otherwise indicated, are from the Lucidol Div., Wallace and Tiernan.

The structure of methylethylketone peroxide is:



The market product has about 11% active oxygen.

Stability: Lupersol loses about 7% of its peroxide content after 12 months of storage at ambient temperatures (20–80°F).

DECOMPOSITION KINETICS

Active %	Conc. g. moles peroxide (–O–O–)/l.	Temp. °C	Half Life $t_{1/2}$ in hrs.	First Order Rate k /hr.	E (Activation Energy) Kcal./mole
11 at start	8.2	85	81.2	0.00854	
		100	16.2	0.0428	
		115	3.6	0.193	28.5
		145	0.25	2.77	

DECOMPOSITION TEMPERATURES IN BENZENES AT SELECTED HALF LIFE VALUES

Time	1 min.	10 hrs.	100 hrs.
Temp. C°	182	105	83

Solubility Data : Soluble in most synthetic resin monomers.

Health Hazard : Highly toxic by ingestion.

Safety Classifications:

OSM: Not specifically listed but peroxides are in class 1 when stored in original shipping containers, and in class 2 when not in original shipping containers or the equivalent.

ICC: Not specifically listed, but organic peroxides not otherwise specified are classed as flammable liquids and as oxidizing materials under "Explosives and Other Dangerous Articles."

Fire and Explosion Hazard : Methylethylketone peroxide alone is shock sensitive. To reduce the sensitivity to shock, it is diluted with dibutylphthalate and is then acceptable for shipment. The peroxide may exist in several different structures, some of which are extremely shock sensitive even in 60% solution. The solution may thus be a hazard. Lupersol DDM will decompose rapidly at 125°C. The solution has a flash point (open cup) above 45°C and burns like gasoline when ignited. Eupersol DDM is widely used

Refs.

Addnl. Ref. 2

Addnl. Ref. 1

Addnl. Ref. 2

Addnl. Ref. 2

12

12, Addnl.
Ref. 3

Lupersol DDM (page 2)

as a ~~room~~ temperature catalyst with cobalt naphthenate or similar metallic drier ~~as the~~ accelerator. Mixtures of the peroxide and accelerator will decompose explosively and the two should not ~~be~~ brought into direct **contact**. ~~As~~ a powerful oxidizing agent, the peroxide ~~can~~ react **vigorously** with reducing materials.

Storage Precautions: **Store** in an isolated building with no other ~~type~~ of material. Buildings containing the peroxide should be posted "Flammable Storage—Keep Fire Away."

Disposal of **Lupersol DDM**: Burning, the preferred method, or **chemical** hydrolysis.

Burning Method: Pour material to be destroyed into shallow trench. Ignite with a wadded gasoline soaked rag tied to the end of a 6-ft. steel rod. Boiling will be rapid but not violent.

Chemical Hydrolysis Method: Slowly add peroxide solution to 10 times its weight of 20% NaOH solution with constant stirring. The reaction is exothermic. Decomposition ~~shall~~ be complete in 24 hours, and is confirmed when an acidified sample of the alkaline reaction mixture does not liberate iodine from an acetone solution of NaI.

Electrostatic Sensitivity: ———

Use in Pyrotechnics: Usually with cobalt naphthenate (g.v.) to cure **Laminac 4116** (see PA-PD-594).

Additional References:

- 1) Chem. Eng. News (Dec. 7, 1959) (Wallace and Tieman advertisement).
- 2) "The Evaluation of Organic Peroxides on the Basis of Half Life Data," D. Doehnert and O. Mageli, **Modern Plastics** 86, 142 (1959)
- 3) "The Use of Organic Peroxides," C. H. Rybolt, paper presented at the 11th meeting of The Reinforced Plastics Division, S.P.I., Atlantic City, New Jersey (1956)
- 4) For use with Laminac 4116, see Ref. 73

Addnl. Ref. 3

MAGNESIUM, Mg

Refs.

Specification No. :

3AN-M-382

The specification covers three types. Types I and II must be manufactured by grinding, scamping, turning, or any combination of these methods which will yield a suitable product. Type III must be manufactured by the atomizing process. Type I is divided into two grades which differ in purity. Type I, grade A, and types II and III all have the same purity requirements. Grade B is ordinarily manufactured from scrap.

Molecular Weight :

24.32

Crystalline Form :

hexagonal

Color :

silvery white

Density, g./ml. :

1.74

Coefficient of Thermal Expansion at 20–100°C :

26×10^{-6}

Temp. °C

Coeff.

–183 to +15

21.40×10^{-6}

20–200

27.9×10^{-6}

20–500

29.8×10^{-6}

Heat of Formation, Kcal./mole at 298°K :

(gas) 35.6

Free Energy of Formation, Kcal./mole at 298°K :

(gas) –27.341

Entropy, cal./deg./mole at 298°K :

(c) 7.81

(gas) 35.51

See Tables a and b

Melting Point :

923°K (650°C)

Heat of Fusion, cal./mole :

2140

Boiling Point :

1390°K (1117°C)

Heat of Vaporization, cal./mole :

30,750

Transition Point :

Heat of Sublimation, cal./mole at 298°K :

35,600

Heat Content or Enthalpy, cal./mole at 298°K :

1195

a. HEAT CONTENT AND ENTROPY OF Mg (c, l)
(Base, ideal gas at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	615	1.78	923 (l) . . .	6415	9.86
500	1255	3.20	1000	7020	10.48
600	1920	4.41	1100	7800	11.23
700	2610	5.48	1200	8580	11.91
800	3330	6.44	1300	9360	12.53
900	4095	7.34	1400	10,140	13.11
923 (c) . . .	4275	7.54			

Mg (c) :

Enthalpy: $H_T - H_{298.15} = 4.97T + 1.52 \times 10^{-3}T^2 - 0.04 \times 10^5T^{-1} - 1604$ (0.2 percent ;298–923°K)

Heat Capacity: $C_p = 4.97 + 3.04 \times 10^{-3}T + 0.04 \times 10^5T^{-2}$

$$\text{Enthalpy: } H_T - H_{298.15} = 7.80T - 780 \text{ (0.1 percent; 923-1400}^\circ\text{K)}$$

4

$T, ^\circ K$	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	$T, ^\circ K$	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	505	1.46	1900	7960	18.20
500	1005	2.57	2000	8455	18.46
600	1500	3.46	2200	9450	19.93
700	1995	4.24	2400	10,445	20.36
800	2495	4.90	2600	11,440	20.76
900	2990	5.49	2800	12,440	21.13
1000	3490	6.01	3000	13,440	21.48
1100	3985	6.49	3500	16,980	22.26
1200	4480	6.92	4000	18,610	22.96
1300	4980	7.32	4500	21,400	23.62
1400	5475	7.69	5000	24,410	24.25
1500	5970	8.03	6000	31,355	25.52
1600	6470	8.35	7000	39,955	26.84
1700	6965	8.65	8000	50,805	28.28
1800	7465	8.93			

$$\text{Enthalpy: } H_T - H_{298.15} = 4.971' - 1482 \text{ (0.2 percent; } 298\text{--}3500^\circ\text{K)}$$

(solid)	6.96
(liquid)	7.80
(gas)	4.97

6

Solid 298–923°K	
Liquid 923–1390°K	
Gas (mon) 1390–3000°K	
T, °K	C _p (cal./deg./mole)
298	5.96
400	6.24
600	6.76
800	7.42
900	7.81
1000	7.88
1100	8.14
1200	8.40
1300	8.66
1400 to	
2400	4.97
2500	4.98
3000	5.02

Magnesium, Mg (page 3)Decomposition Temperature and **Products** :For **TGA** see Addnl. Ref. 7For **TGA** and **DTA** see also Ref. 33

Vapor Pressure :

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	621	743	838	909	1034	1107	651

X-Ray Crystallographic Data :

System	Space Group	a	c	Atoms/Unit Cell
hexagonal	D _{6h} ⁴	3.203	5.196	2

Hygroscopicity : slowly oxidizes in moist air

Grade B material (see Spec. grades)	R.H. at 70°F	Time of Exposure, hrs.	Gain in weight, %
	50	216	0.06
	70	216	0.22
	90	168	0.62

Solubility Data: Insoluble in cold water; slightly soluble in hot; decomposing to Mg (OH)₂. Soluble in mineral acids (except CrO₃), conc. HF, NH₄ salts. Insoluble in alkalis. Reacts readily with dilute acids with evolution of hydrogen.

Health Hazard : Slightly to moderately toxic. Particles which perforate the skin may produce severe local tumors characterized by the formation of pockets of gas and acute inflammatory reaction, frequently with necrosis (chemical gas gangrene). Inhalation of fumes or dust may irritate the respiratory tract.

M.A.C. : 10 pts. per million in air and 15 mg./m.³ of fumes as MgO.

Safety Classifications :

OSM : **Class 1** ; class 2 when not stored in original shipping containers or equivalent.

ICC : Magnesium scrap (shavings, borings or turnings) is classed as a flammable solid ;yellow label.

Fire and Explosion Hazard: Contact with water may cause ignition of powdered magnesium evolution of hydrogen, and explosion. Dangerous in the form of dust or flakes when exposed to flame or by chemical action with an oxidizing agent. Finely divided magnesium can be ignited by a spark or match flame. Highly explosive. Caution : water, CO₂, or carbon tetrachloride should not be used on magnesium fires. Use G-1 powder or powdered talc on open fires and boron trichloride on oven fires.

Store and process only in rooms or buildings adequately vented at the highest point to prevent the accumulation of hydrogen gas which results from the reaction of powdered metal and moisture. In the repair and maintenance of buildings or equipment, powder or dust should be removed and non sparking tools used.

Magnesium, Mg (page 4)

Electrostatic Sensitivity : Minimum energy required for ignition of powder by electric sparks (millijoules) :

<i>Type</i>	<i>Dust Layer</i>	<i>Cloud Layer</i>	
atomized	120	40	26, 51
milled	40	8	
stamped	20	1	

Can be ignited by a spark in an atmosphere of CO₂ or in air-nitrogen mixtures with not less than 3% oxygen. To avoid ignition process in helium.

Ignition Temperatures of Magnesium Powders, °C :

<i>Type</i>	<i>Dust Cloud</i>	<i>Dust Layer</i>	
atomized	600	490	
milled	540	475	
stamped	520	480	

Minimum Explosive Concentration, mg./l. : (atomized) 10
(milled) 20
(stamped) 20

Use in Pyrotechnics : As a fuel, and in tracer, igniter, signal flare, and pyrotechnic compositions.

Additional References :

- 1) "The Kinetics of Underwater Corrosion of Powdered Magnesium," E. Freeman and S. Gordon, *J. Phys. Chem.* **50**, 1009 (1955)
- 2) "Magnesium and Its Alloys," C. S. Roberts, John Wiley & Sons, New York (1960)
- 3) "National Fire Codes, Vol. II, The Prevention of Dust Explosions," National Fire Protection Association, Boston, Mass. (1952)
- 4) "Safety Requirements for Manufacturing and Processing Military Pyrotechnics," **ORDM 7-255** (1952)
- 5) *C.A.* **37**, 2578 (1943)
- 6) Ref. 64
- 7) *Combustion and Flame* **3**, No. 1, 3-12 (1959)

MAGNESIUM-ALUMINUM ALLOY (Magnalium)

Refs.

Specification No. : JAN-M-454

The specification covers two types, A and B, which differ in granulation (B is coarser) : A = 50/50 Mg/Al, approx. 53.3 atom % Mg.
B = 66/35 Mg/Al, approx. 67.0 atom % Mg.

spec.

Molecular Weight :

Color and Form:

silvery metal

Density, g./ml. :

(solid) type A, about 2.142
type B, about 2.015

Calculated on the basis of data in Addnl. Ref. 3

Coefficient of Thermal Expansion :

type A, approx. 29.3×10^{-6}
type B, approx. 28.7×10^{-6}

By interpolation from Addnl. Ref. 2

Heat of Formation, cal./mole at 298°K:

type A, -1027

24

Boiling Point : Decreases with increasing Mg content.

44S35

Wt. % Mg	20	40	60	80
B.P. °C	1300	1200	1150	1116

Vapor Pressure: See Addnl. Refs. 2 and 4

X-Ray Crystallographic Data:

	<i>a</i>	Atoms/Unit Cell
type A	about 10.46	about 58
type B	about 10.57	about 58

By interpolation and extrapolation of data in Addnl. Ref. 3

Hygroscopicity: Cumulative increase in weight after storage :

over water for 29 days	over H ₂ SO ₄ for 29 days	2 days in oven at 105°C
6.3%	4.7%	4.3%

51

Solubility Data:

see Magnesium and Aluminum

Health Hazard:

no known toxicity

50V8

Safety Classifications:

OSM: No classification given. Since Al and Mg powders are in class 1, powdered Mg/Al alloy is probably similarly classified.

ICC: No classification given. However, since powdered metallic magnesium is classified under "Explosives and Other Dangerous Articles," the alloy would be similarly classified as a flammable solid requiring a yellow label.

Fire and Explosion Hazard: Prevent water from contacting the powdered material. Store and process only in rooms or buildings adequately vented at the highest point to prevent the accumulation of hydrogen gas which results from the reaction of powdered metal and moisture. Powdered Mg/Al alloy mixed with oxidizing agents is a dangerous fire and explosion hazard. Powdered metal exposed to the air is a dangerous fire hazard, and when ignited burns with intense heat. In the repair or maintenance of buildings or equipment, powder or dust should be removed and nonsparking tools used.

14

Minimum Explosive Concentration of type A Mg/Al powder is 50 mg./l.

26

Magnesium-Aluminium (magnalium) (page 2)

Electrostatic Sensitivity: Minimum energy required for ignition of powder by electric sparks, millijoules :	(dust cloud) 80	26, 50
	(dustlayer) 20	
Ignition Temperature, °C of type A alloy:	(dust cloud) 535	26, 50
	(dustlayer) 46	
Use in Pyrotechnics:	as fuels	

Additional References:

- 1) "Magnesium and Its Alloys," by C. S. Roberts, John Wiley & Sons, New York (1960)
- 2) "The Physical Metallurgy of Magnesium and its Alloys," G. V. Raynor, Pergamon Press, New York (1959). Contains a *good* phase diagram of the system Mg/Al, plus a discussion.
- 3) "Handbook of Lattice ~~Spacings~~ and Structures of Metals," W. B. Pearson, Pergamon Press, New York (1958)
- 4) A. Schneider and E. H. Stroll, Z. Electrochem. 47, 519 (1941)

MAGNESIUM CARBONATE, MgCO_3

Refs.

Specification No. :	MIL-M-11361	
Molecular Weight:	84.33	
Crystalline Form :	trigonal	1
Color :	white	1
Density, g./ml. :	(solid) 3.037	1
Coefficient of Thermal Expansion, cubical :	0.5×10^{-7}	31
Heat of Formation, Kcal./mole at 298°K :	-266	1, 9
Free Energy of Formation, Kcal./mole at 298°K :	-246	1, 9
Entropy, cal./deg./mole at 298°K :	15.7	1, 9
See table below		
Melting Point :	decomposes at 623°K (350°C)	1
Heat of Fusion :	—	
Boiling Point:	loses CO_2 at 1173°K (900°C)	1
Transition Point :	—	
Heat of Sublimation :	—	

HEAT CONTENT AND ENTROPY OF MgCO_3 (c) (Base, crystals at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	2060	5.92	700	9450	19.54
500	4300	10.91	750	10,820	21.43
600	6790	15.45			

Enthalpy: $H_T - H_{298.15} = 18.62 + 6.90 \times 10^{-3}T^2 + 4.16 \times 10^{-5}T^3 - 7560$
(0.4 percent ; 298-750°K)

Heat Capacity: $C_p = 18.62 + 13.80 \times 10^{-3}T - 4.16 \times 10^{-5}T^2$

Heat Capacity, cal./deg./mole : (solid) 18.05

Decomposition Temperature : 900°C

For TGA see Addnl. Ref. 1

Magnesite (mineral MgCO_3) begins to lose CO_2 at 450-500°C

Decomposition Products : $\text{MgO} + \text{CO}_2$

Vapor Pressure :

Press. atm.	.0001	.0089	.0776	0.983	1.763	13.87	473.4
Temp. °K	673.1	723.1	763.1	813.1	843.1*	873.1*	973.1*

*calculated from equation

$$\log kp_1 - \log kp_2 = \frac{\Delta H (T - T_2)}{4.571 (T \cdot T_2)}, \Delta H = 60.863$$

9
64

50V5

29

42V7

Magnesium Carbonate, MgCO₃ (page 2)

X-Ray Crystallographic Data :

<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>Axial Angle</i>	<i>Molecules/ Unit Cell</i>	
hexagonal	D _{3d} ⁶	5.61	$\alpha = 48^\circ 12'$	2	1
Hygroscopicity :					
Solubility Data: In water :			.0106 g./100 ml.		1, 29
More soluble in water containing CO ₂ .					
In acids:			soluble, reacts with evolution of CO ₂		
In acetone, NH ₃ , and alcohol:			insoluble		
Health Hazard : None. Has an antacid and laxative effect. Slight to moderate on ingestion and inhalation.					29, 93
Safety Classifications :			_____		
Fire and Explosion Hazard:			_____		
Electrostatic Sensitivity :			_____		
Use in Pyrotechnics :			as a retardant		
Additional References :					
1) J. Am. Ceram. Soc. 33, 96101 (1950)					

MAGNESIUM OXIDE, MgO

(Magnesia, Calcined Magnesia, Dead Burned Magnesia, Light Magnesia,
Ponderous Magnesia, Magnesia Usta Periclase)

Specification No.:	MIL-M-12036A	Refs.
The spec. covers one grade of MgO, light (technical).		1, 11, 29
Molecular Weight:	40.32	
Crystalline Form:	cubic	1
The spec. grade is a fluffy white amorphous powder.		
Color:	colorless	1
Density, g./ml.:	(solid) 3.58	1
Coefficient of Thermal Expansion, linear, 20–500°C :	12.4×10^{-6}	
	20–1000°C : 13.7×10^{-6}	27
	25°C : 14.45×10^{-6}	97V1
Thermodynamic Data for finely divided MgO :		9
See also Tables a and b		
Heat of Formation, Kcal./mole at 298°K:	-142.95	
See Table a		
Free Energy of Formation, Kcal./mole at 298°K :	-135.31	
Entropy, cal./deg./mole at 298°K :	6.66	
Heat Capacity, cal./deg./mole at 298°K :	9.03	
See Table b		
a. HEAT AND FREE ENERGY OF FORMATION OF MgO (periclase)		2, 8

T, °K	ΔH (cal./mole)	ΔF° (cal./mole)
298.16	-143,800(± 90)	-136,080(± 150)
400	-143,810	-134,530
500	-143,810	-130,860
600	-143,810	-128,270
700	-143,800	-125,680
800	-143,790	-123,080
900	-113,773	-120,430
923	-143,760	-119,890
923	-145,920	-119,890
1000	-145,890	-117,730
1100	-145,840	-114,910
1200	-145,750	-112,100
1300	-145,660	-109,300
1393	-145,560	-106,690
1393	-177,060	-106,690
1400	-177,030	-106,350
1500	-176,700	-101,300
1600	-176,380	-96,280
1700	-176,060	-91,300
1800	-175,740	-86,330
1900	-175,420	-81,370
2000	-175,100	-76,400

Magnesium Oxide, MgO (page 2)

Phase Changes of Metal

M.P., 923°K; $\Delta H = 2160$ cal./g.-atom

B.P., 1393°K; $\Delta H = 31,500$ cal./g.-atom

Free Energy Equations:

Reaction	Range of Validity, °K	
1) $\text{Mg (c)} + \frac{1}{2} \text{O}_2 = \text{MgO (periclase)}$	298.16-923	
$\Delta F_T^\circ = -144,090 - 1.06T \log T - .13 (10^{-3}T^2) + .25 (10^5T^{-1}) + 29.16T$		
2) $\text{Mg (l)} + \frac{1}{2} \text{O}_2 = \text{MgO (periclase)}$	923-1393	
$\Delta F_T^\circ = -146,810 + 1.84T \log T - .62 (10^{-3}T^2) + .64 (10^5T^{-1}) + 23.07T$		
3) $\text{Mg (g)} + \frac{1}{2} \text{O}_2 = \text{MgO (periclase)}$	1393-2000	
$\Delta F_T^\circ = -180,700 - 3.75T \log T - .62 (10^{-3}T^2) + .64 (10^5T^{-1}) + 65.69T$		
Entropy, cal./deg./mole at 298°K:	6.4	1, 9
See Table b		
Melting Point:	3173°K (2900°C)	9
Heat of Fusion, Kcal./mole:	18.5	9
Boiling Point:	3350 $\pm$ 300°K (3077°C)	8
Heat of Vaporization:	—	
Transition Point:	—	
Heat of Sublimation, Kcal./mole at 298°K:	> 149.4	64
		4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	965	2.78	1300	11,310	15.98
500	1975	5.03	1400	12,570	16.92
600	3020	6.94	1500	13,830	17.79
700	4100	8.60	1600	15,090	18.60
800	5225	10.10	1700	16,350	19.36
900	6390	11.47	1800	17,610	20.08
1000	7580	12.73	1900	18,870	20.76
1100	8800	13.89	2000	20,130	21.41
1200	10,050	14.98	2100	21,390	22.02

MgO (c):

Enthalpy: $H_T - H_{298.15} = 10.18T + 0.87 \times 10^{-3}T^2 + 1.48 \times 10^5T^{-1} - 3690$
(0.8 percent; 298-2100°K)

Heat Capacity: $C_p = 10.18 + 1.74 \times 10^{-3}T - 1.48 \times 10^5T^{-2}$

Heat Capacity, cal./deg./mole: (solid, c) 8.94

See equation above

9

Magnesium Oxide, MgO (page 3)

Decomposition Temperature. The temperature required to complete dissociation has been estimated to be above that of the temperature of a Bunsen flame. Partial dissociation is said to take place by evaporating a mixture of MgO and metal.

44V27B

Decomposition Products :

Vapor Pressure : $\log_{10} P_{\text{mm.}} = 2.732 \times 10^4/T + 13.13$, over the temperature range 1800–2200°K

Addnl. Refs.
1, 3

X-Ray Crystallographic Data :

<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>Molecules/Unit Cell</i>
cubic	O_h	4.212	4

97V1

Hygroscopicity: Takes up moisture from the air to form Mg(OH)_2 and CO_2 from the air to form MgCO_3 .

Caution : Keep container well closed.

29

See also Addnl. Ref. 2.

Solubility Data: In water:

.00062 in cold

1

.0086 at 30°C

29

Solubility in water is increased by CO_2 .

In acids and ammonium salts:

soluble

In alcohol:

insoluble

Health Hazard: inhalation of freshly sublimed MgO may cause metal fume fever. Large doses taken as an antacid may produce undesirable catharsis.

12

29

M.A.C., mg./m.³ for an 8-hr. day :

15

14

Safety Classifications :

OSM:

not listed

ICC:

not listed

Fire and Explosion Hazard:

—

Electrostatic Sensitivity:

—

Use in Pyrotechnics: MgO is the product of the burning of Mg.

Additional References :

- 1) "Stability of Ceramic Materials," J. Wygant and W. Kingrey, Am. Ceram. Soc. Bull. 31, (7) 251 (1952); cited by Ref. 65
- 2) "The Sorption of Water Vapor on Magnesium Oxide," R. Razouk and R. Sh. Mikhail, J. Yhys. Chem. 59, 636 (1955)
- 3) "On the Dissociation Energies of Strontium Oxide and Magnesium Oxygen Molecules," R. Porter et al., J. Chem. Phys. 23, 1347 (1955)

MANGANESE, Mn

Refs.

Specification No. :

JAN-M-476

The specification covers three grades which differ in purity and granulation. Grade I is intended for delay powder; grades II and III, for pyrotechnics.

Molecular Weight :

54.94

Crystalline Form :

cubic or tetragonal

Color :

grey-pink

Density, g./ml. :

(solid at R.T.) $\alpha = 7.44$
 $\beta = 7.29$
 $\gamma = 7.21$

1

1

37

Coefficient of Thermal Expansion, linear :

	Temp. ($^{\circ}C$)	Coeff. (cm./cm./ $^{\circ}C$)
α phase	-190 to 0	15.9×10^{-6}
	-183 to 0	17.6×10^{-6}
	0-20	22.3×10^{-6}
	0-100	22.8×10^{-6}
	0-300	25.2×10^{-6}
β phase	-183 to 0	$12.8-20.4 \times 10^{-6}$
	0-20	$18.7-24.9 \times 10^{-6}$
γ phase	-70 to 0	13.6×10^{-6}
	0-20	14.8×10^{-6}

27, 37

Heat of Formation, Kcal./mole at 298 $^{\circ}K$:

(gas) 68.34
(c) γ , 0.37

1, 5

Free Energy of Formation, Kcal./mole at 298 $^{\circ}K$:

(gas) 58.23
(c) γ , 0.37

1, 5

Entropy, cal./deg./mole at 298 $^{\circ}K$:

(gas) 41.49
(c) α , 7.59
 γ , 7.72

1

See Tables a, b, c, d

Melting Point :

1517 $^{\circ}K$ (1244 $^{\circ}C$)

2, 5

Heat of Fusion, cal./mole:

3500

2, 4, 5

Boiling Point:

2314 $^{\circ}K$ (2041 $^{\circ}C$)

5

Heat of Vaporization, cal./mole at 2314 $^{\circ}K$:

52,520

5

Transition Points :

α $\xrightarrow{(727^{\circ}C) \rightarrow 1000^{\circ}K}$ β $\xrightarrow{(1101^{\circ}C) \rightarrow 1374^{\circ}K}$ γ $\xrightarrow{(1137^{\circ}C) \rightarrow 1410^{\circ}K}$ δ

2, 4, 5

Heat of Transition, cal./mole :

$\alpha \xrightarrow{535} \beta \xrightarrow{545} \gamma \xrightarrow{430} \delta$

2, 4, 5

Heat of Sublimation, cal./mole at 298 $^{\circ}K$:

66,730

5

Heat Content or Enthalpy, cal./mole at 298 $^{\circ}K$: See Tables a, b, c, d

Heat Capacity, cal./mole at 298 $^{\circ}K$: See Tables a, b, c, d

a. HEAT CONTENT AND ENTROPY OF Mn (c, 1)
(Base, α -crystals at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	690	1.99	1410 (γ) . . .	10,330	13.21
500	1385	3.54	1410 (δ) . . .	10,760	13.51
600	2120	4.88	1500	11,780	14.21
700	2895	6.07	1517 (δ) . . .	11,970	14.34
800	3715	7.16	1517 (l) . . .	15,470	16.65
900	4570	8.17	1600	16,380	17.23
1000 (a) . . .	5450	9.10	1700	17,480	17.90
1000 (β) . . .	5985	9.63	1800	18,580	18.53
1100	6890	10.50	1900	19,680	19.12
1200	7795	11.28	2000	20,780	19.69
1300	8715	12.02	2100	21,880	20.22
1374 (β) . . .	9395	12.53	2200	22,980	20.74
1374 (γ) . . .	9940	12.93	2300	24,080	21.22
1400	18,220	13.13			

Mn (a) :

$$\text{Enthalpy: } H_T - H_{298.15} = 5.709T + 1.69 \times 10^{-5}T^2 + 0.37 \times 10^{-5}T^{-1} - 1974$$

(0.7percent ;298-1000°K)

$$\text{Heat Capacity: } C_p = 5.70 + 3.38 \times 10^{-5}T - 0.37 \times 10^{-5}T^{-2}$$

Mn (β) :

$$\text{Enthalpy: } H_T - H_{298.15} = 8.33T + 0.33 \times 10^{-5}T^2 - 2675 \text{ (0.1percent ;1000-1374°K)}$$

$$\text{Heat Capacity: } C_p = 8.33 + 0.66 \times 10^{-5}T$$

Mn (γ) :

$$\text{Enthalpy: } H_T - H_{298.15} = 10.70T - 4760 \text{ (0.1percent; 1374-1410°K)}$$

$$\text{Heat Capacity: } C_p = 10.70$$

Mn (δ) :

$$\text{Enthalpy: } H_T - H_{298.15} = 11.30T - 5170 \text{ (0.1percent ;1410-1517°K)}$$

$$\text{Heat Capacity: } C_p = 11.30$$

Mn (l) :

$$\text{Enthalpy: } H_T - H_{298.15} = 11.00T - 1220 \text{ (0.1percent; 1517-2300°K)}$$

$$\text{Heat Capacity: } C_p = 11.00$$

Manganese, Mn (page*3)

b. HEAT CONTENT AND ENTROPY OF Mn (γ)
(Base, γ -crystals at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	705	2.03	1000	5750	9.57
500	1445	3.68	1100	6720	10.50
600	2230	5.11	1200	7730	11.38
700	3050	6.38	1300	8780	12.22
800	3915	7.53	1374	9570	12.81
900	4815	8.59			

Mn (γ) :Enthalpy : $H_T - H_{298.15} = 6.03T + 1.78 \times 10^{-5}T^2 + 0.44 \times 10^{-5}T^{-1} - 2104$
(0.1 percent ; 298-1374°K)Heat Capacity : $C_p = 6.03 + 3.56 \times 10^{-5}T - 0.44 \times 10^{-5}T^{-2}$ c. HEAT CONTENT AND ENTROPY OF Mn (g)
(Base, ideal gas at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	505	1.46	1900	7960	9.20
500	1005	2.57	2000	8460	9.46
600	1500	3.48	2200	9455	9.93
700	1995	4.24	2400	10,455	10.37
800	2495	4.90	2600	11,465	10.77
900	2990	5.49	2800	12,485	11.15
1000	3490	6.01	3000	13,525	11.51
1100	3985	6.49	3500	16,255	12.35
1200	4480	6.92	4000	19,290	13.16
1300	4980	7.32	4500	22,775	13.98
1400	5475	7.68	5000	26,840	14.84
1500	5970	8.03	6000	36,925	16.69
1600	6470	8.35	7000	49,415	18.59
1700	6965	8.93	8000	63,560	20.48
1800	7465				

Manganese, Mn (page 4)

d. HEAT CAPACITY OF Mn:

Solid I, 298-1000°K; Solid II, 1000-1374°K :
Liquid, 1517-2314°K; Gas (monatomic) 2314-3000°K

T, °K	C _p (cal./deg./mole)	T, °K	C _p (cal./deg./mole)
298	6.29	1400	10.70
400	6.75	1500	11.30
600	7.54	1600 ^b	11.00
		2300	
800	8.21	2400	5.02
900	8.60	2600	6.07
1000 to	9.30	2800	5.14
1300		3000	6.26

Decomposition Temperature and **Products** :

For **DTA** and **TGA** see **Ref.** 33

Vapor Pressure :

Press. mm.	1	P0	40	100	400	760	M.P.
Temp. °C	1292	1505	1666	1792	2029	2151	1260

$\log P (\sim \text{mm.}) = 14,848T - 3.023 \log T + 16,489T$ (T = abs. temp.)
2.4 mm. at M.P.

X-Ray Crystallographic Data :

System	Space Group	a	c	Atoms/ Unit Cell
cubic (α)	F _m	8.894		58
cubic (β)	O _h or O _h	6.300		20
tetragonal (γ)	D _{4h}	3.774	3.526	4
cubic (δ)		3.081 at 1140°C	3.088 at M.P.	

Hygroscopicity (% Gain in weight after 720 hrs. of exposure at 70°F of spec. grade powdered Mn) :

R.H., %	50	76	90
Gain, %	0.02	0.34	3.91

Solubility Data : Decomposes water slowly in the cold, rapidly on heating.

Soluble in dilute acids with evolution of hydrogen.

Health Hazard : Inhalation of heavy concentrations of manganese **dusts** or **fumes** may produce chronic manganese **poisoning**. **Mn** may affect the nervous system and cause paralysis. Mn poisoning is detectable in the blood.

M.A.C., mg./m.³ : 6

Safety Classifications :

OSM: Class 2, when not packed or stored in the original shipping container or equivalent (dust).

ICC : not specifically mentioned

Manganese, Mn (page 5)

Fire and Explosion Hazard: Powdered manganese metal exposed to air is a dangerous fire hazard and when ignited burns with intense heat. Prevent water from contacting the material. Store and process only in buildings adequately vented at the highest point to prevent the accumulation of hydrogen gas which results from the reaction of powdered metal and moisture. In the presence of oxidizing agents powdered Mn is a dangerous fire and explosion hazard. Manganese powder is moderately explosive.	12, 14, 49
Caution: to fight fire, use a special mixture of dry chemical or powdered talc. Use nonsparking tools for repair and maintenance of buildings or equipment where manganese has been stored.	51, 75
Electrostatic Sensitivity : Minimum energy required for ignition of powder by electric sparks (millijoules) : $\gamma \pm 0.77\%$ $\delta \pm 0.90\%$	26
Minimum explosive concentration of powdered Mn : 125 mg./l.	26
Volume change accompanying phase transformations : $\beta \rightarrow \gamma \pm 0.77\%$ $\gamma \rightarrow \delta \pm 0.90\%$	37
Manganese is superficially oxidized on exposure to the air. The γ phase (electrolytic Mn) is not attacked by water at ordinary temperatures. It is slightly attacked by steam.	29
Use in Pyrotechnics : as a fuel	

MANGANESE DIOXIDE, MnO₂
(Manganese Black, Pyrolusite, Black Oxide of Manganese,

Re/s.
1, 11, 29

Crystalline Form:	rhombic or powder	1
Color:	black or brownish-black	1
Density, g./ml.:	(solid) 5.026	
Coefficient of Thermal Expansion:	—	
Heat of Formation, Kcal./mole at 298°K:	-124.5	1, 9
See Table a		
Free Energy of Formation, Kcal./mole at 298°K:	-111.4	1, 9
See Table a		

a. HEAT AND FREE ENERGY OF FORMATION **MnO₂ (c)**

K	Δ H (cal./mole)	Δ F° (cal./mole)
298.16	-124,450 (± 200)	-111,350 (± 250)
400	-124,400	-106,900
500	-124,250	-102,500
600	-124,100	-98,200
700	-123,900	-93,900
800	-123,750	-89,600
900	-123,650	-85,350
1000	-123,500	-81,100

Free Energy Equation:

$$\begin{array}{l} \text{Reaction} \\ \text{Mn (s)} + \text{O}_2 \text{ (g)} = \text{MnO}_2 \text{ (c)} \\ \Delta F^\circ = 126,400 - 8.61T \log T + .97 (10^{-8}T^2) + 1.555 (10^{-5}T^{-1}) + 70.14T \end{array}$$

Range of Validity, °K

298.16–1000

Entropy, cal./deg./mole at 298°K:

12.7

See Table b

Melting Point:

loses oxygen at

1120°K (847°C)

loses oxygen at 535°C

Heat of Fusion:

Boiling Point:

Transition Point:

Heat of Sublimation:

Manganese Dioxide, MnO₂ (page 2)

b. HEAT CONTENT AND ENTROPY OF MnO₂ (c)
(Base, crystals at 298.15°K)

4

<i>T</i> , °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	<i>T</i> , °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	1445	4.16	700	6415	13.36
500	3020	7.67	800	8185	15.73
600	4685	10.70			

MnO₂ (c) :

Enthalpy : $H_T - H_{298.15} = 16.60T + 1.22 \times 10^{-5}T^2 + 3.88 \times 10^5T^{-1} - 6359$
(0.1 percent ; 298–800°K)

Heat Capacity : $C_p = 16.60 + 2.44 \times 10^{-5}T - 3.88 \times 10^5T^{-2}$

Heat Capacity, cal./deg./mole : (solid) 12.91

Decomposition Temperature, °K : 1120

For DTA see Ref. 33

Decomposition Products : Loses O when heated ; the temperature of decomposition varying with the method of preparation from 530°C down to even 200°C. The resulting products being successively **Mn₂O₃**, **Mn₃O₄**, and **MnO**. The reactions are reversible.

Dissociation Pressure : $2 \text{ MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 (\text{s}) + \frac{1}{2} \text{ O}_2 (\text{g})$

Press. atm.	0.030	0.164	0.263	0.209	1.36	1.000
<i>T</i> , °K	655.1	721.1	751.1	803.1	809.1	1213.1

X-Ray Crystallographic Data :

System	Space Group	<i>a</i>	<i>c</i>	Molecules/ Unit Cell
tetragonal	D _{4h} ¹⁴	4.44	2.89	2

Hygroscopicity :

Solubility Data: In water, HNO₃, cold H₂SO₄, acetone:

In HCl with evolution of Cl: insoluble
soluble

Health Hazard : Continued or prolonged inhalation or exposure to heavy concentrations of MnO₂ dusts or fumes may cause chronic manganese poisoning. The chief site of damage is the central nervous system. Although toxic when freshly formed, the dry crystals or powder are normally considered an eye irritant and toxic only in large quantities. In solution, manganese dioxide forms a strong base that may burn the skin, and is very irritating to the eyes.

M.A.C. mg./m.³ : 6

Safety Classifications :

OSM : Class I. Class 2 when not packed or stored in original shipping containers or equivalent.

ICC : oxidizing material
Coast Guard : hazardous material

Manganese Dioxide, MnO_2 (page 3)

Fire and Explosion Hazard: A strong oxidizer and a fire hazard in the finely

29

phites.

Precautions When Handling Manganese Dioxide :

Work carefully when handling bulk manganese dioxide to avoid excessive "dusting." Keep work areas clean, and wash hands frequently. Store away from readily oxidizable materials such as powdered metals, oils, acids, or organic solvents.

A solution of one part vinegar to four parts water by volume is an effective neutralizer, and may be safely used in the eyes or on any part of the skin. Take a victim to a physician immediately for examination and further treatment.

Electrostatic Sensitivity :

Use in Pyrotechnics:

as an oxidizer

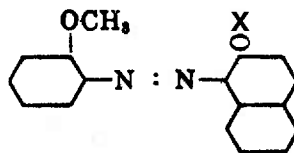
17

1-(2-METHOXYPHENYLAZO)-2-NAPHTHOL
(2-anisole-azo-betanaphthol, Sudan Red G, Brilliant Fat Scarlet R,
C.I. 12150, C.I. Solvent Red I, C.I. Food Red 16)

Refs.

48A

Formula : $C_{17}H_{14}N_2O_2$



Specification No. :

MIL-D-3179

The spec. covers two grades differing in purity (grade I, 90% ; grade II 80%) and granulation.

Molecular Weight :

278.32

Crystalline Form :

needles

Color :

shiny reddish-yellow

38V16

Density, g./ml. :

Apparent Density (spec. grade I)

min. 0.30, max. 0.70

Coefficient of Thermal Expansion :

Heat of Formation :

Free Energy of Formation :

Entropy :

Melting Point :

451°K (178°C)

88V16

Spec. grade II, min.

448°K (175°C)

Heat of Fusion :

Boiling Point :

Transition Point :

Heat of Sublimation :

Heat Content or Enthalpy

Heat Capacity :

Decomposition Temperature :

Decomposition Products :

Vapor Pressure :

X-Ray Crystallographic Data :

Hygroscopicity :

Solubility Data :

In water, alkalis:

insoluble

In benzene and cold alcohol:

difficult

In alcohol:

red solution on boiling

In $CHCl_3$ and benzene:

fairly soluble

in conc. H_2SO_4 :

soluble with violet-red color

48, 88V16

1-(2-Methoxyphenylazo)-2-Naphthol (page 2)

Health Hazard:

Spec. requires each container be conspicuously labeled, "Caution—Avoid Skin Contact. Use Adequate Ventilation."

toxicity unknown

92

Safety Classifications :

OSM :

not listed

ICC :

not listed

Fire and Explosion Hazard:

Electrostatic Sensitivity:

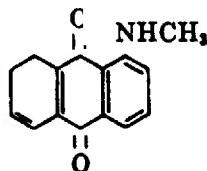
Use in Pyrotechnics:

to color smoke
mixtures red

1-METHYLAMINOANTHRAQUINONE

(1-N-methylaminoanthraquinone, Celliton Pink R, Duranol Red CN,
C.I. 60505, C.I. Disperse Red 9)

Formula: $C_{16}H_{11}NO_2$



Specification No.:	MIL-D-3824	
Spec. covers two grades differing in granulation.		
Molecular Weight:	237.11	
Crystalline Form:	needles	88V14
Color:	yellow-red	84
Density, g./ml.:		
Apparent Density:	(Spec) $0.35 \pm .15$	
Coefficient of Thermal Expansion:	—	
Heat of Formation:	—	
Free Energy of Formation:	—	
Entropy:	—	
Melting Point:	443°K (170°C)	84
Spec. grade II, min.:	442°K (169°C)	
Heat of Fusion:	—	
Boiling Point:	—	
Heat of Vaporization, Kcal./mole at 25°C and 1 atm.:	28.4 ± 0.7	Addnl. Ref. 3
Entropy of Vaporization, vapor at 1 atm., cal./mole/°C:	52.87 ± 0.30	Addnl. Ref. 1
Heat of Sublimation: Kcal./mole:	30.85	Addnl. Ref. 1
Heat Content or Enthalpy:	—	
Heat Capacity:	—	
Decomposition Temperature:		
For TGA see Ref. 80		
Decomposition Products:	—	
Vapor Pressure: $\log_{10}P$ (cm Hg) = $\frac{a}{T} + b$ $a = -6740$; $b = 13.435 \pm 0.036$; $T = \text{abs. temp.}$		Addnl. Ref. 1
Energy of Activation for Volatilization (97% purity), Kcal./mole at 297–376°C:	19.6	80
X-Ray Crystallographic Data:	—	
Hygroscopicity:	—	

1-Methylaminoanthraquinone (page 2)

Solubility Data:

In water, g./100 ml. at 25°C:	<.0002
at 80°C:	0.00055
In alcohol (abs.) at 60°C:	14.96 g./l.
In CHCl ₃ , hot dil. HCl, glacial acetic acid:	soluble
In benzene:	soluble, red
In fuming H ₂ SO ₄ :	soluble, light yellow

Health Hazard:

toxicity unknown

Spec. requires each container be conspicuously labeled, "Caution—Avoid Skin Contact or Breathing of Dust or Fumes. Use with Adequate Ventilation."

Safety Classifications:

OSM:

not listed

ICC:

not listed

Fire and Explosion Hazard:

—

Electrostatic Sensitivity:

—

Use in Pyrotechnics:

to color smoke
mixtures red

Additional References:

- 1) "Vapor Pressures of Some Dispersed Dyes," R. S. Bradley et al., *Nature* **178**, 998 (1956)
- 2) "The Dyeing Phenomena of Acetate Artificial Silk," V. Kartaschoff and G. Farine, *Helv. Chim. Acta.* **11**, 822 (1928)
- 3) "A Radioactive Ionization Gauge and Its Application to the Measurement of Latent Heat of Vaporization," J. H. Benyon and G. R. Nicholson, *J. Sci. Instruments* **33**, 376 (1966)
- 4) For Absorption Spectra see Ref. 66
- 5) *J. Soc. Dyers Colourists* **70**, 68-77 (1964)

Addnl. Ref. 5

92, 88V14 I,
84

92, 93

MOLYBDENUM, Mo

Refs.

Molecular Weight : 95.95
 Crystalline Form : cubic
 Color : silvery-white metal,
 grey-black powder
 Density : (solid) 10.22
 10.24
 9.01

1A

1A

94
 66A
 31A

Coefficient of Thermal Expansion, linear :

Temp, °C	Coeff. $\times 10^6$
20-149	6.43
20-482	5.19
20-649	5.36
20-982	5.80
20-1316	6.28
20-1593	6.65
	4.9

94

$$L = L_0 [1 + (5.01t + 0.00138t^2) \times 10^{-6}]$$

at 20°C : 4×10^{-6}

50V9

31A

See also Refs. 49A* (curve of temp. vs. coeff.), 66A, and Addnl. Refs.

Heat of Formation, Kcal./mole at 298°K : (g) -155.5

9, Addnl.
 Ref. 1

Free Energy of Formation, Kcal./mole at 298°K : (g) -144.2

9, 318

Entropy, cal./deg./mole at 298°K : (g) 43.462
 (c) 6.83

9
 5, 9, 94, 97

a. HEAT CONTENT AND ENTROPY OF Mo (c, 1) (Base, crystals at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	595	1.71	1900	11,200	12.27
500	1205	3.06	2000	12,040	12.70
600	1825	4.20	2100	12,900	13.12
700	2460	5.17 _f	2200	13,770	13.53
800	3100	6.02	2300	14,670	13.92
900	3750	6.79	2400	15,580	14.31
1000	4410	7.49	2500	16,510	14.69
1100	5090	8.13	2600	17,460	15.06
1200	5790	8.74	2700	18,420	15.42
1300	6510	9.31	2800	19,400	15.70
1400	7250	9.85	2890 (c)	20,290	16.09
1500	8000	10.38	2890 (l)	26,940	18.39
1600	8780	10.88	2900	27,040	18.43
1700	9570	11.36	3000	28,040	18.77
1800	10,380	11.82			

Mo (c) :

$$H_T - H_{298.15} = 5.18T + 0.83 \times 10^{-3}T^2 - 1618 \quad (0.5 \text{ percent; } 298-2890^\circ\text{K})$$

$$C_p = 5.18 + 1.66 \times 10^{-3}T$$

Molybdenum, Mo (page 2)

Mo (l) :
 $H_T - H_{298.15} = 10.00T - 1960$ (0.1 percent; 2890-3000°K)

b. HEAT CONTENT AND ENTROPY OF Mo(g)
(Base, ideal gas at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	505	1.46	1500	5975	8.03
500	1005	2.57	1600	6470	8.35
600	1500	3.48	1700	6975	8.66
700	1995	4.24	1800	7475	8.94
800	2495	4.91	1900	7980	9.22
900	2990	5.49	2000	8490	9.48
1000	3485	6.01	2200	9530	9.97
1100	3985	6.49	2400	10,600	10.44
1200	4480	6.92	2600	11,710	10.88
1300	4980	7.32	2800	12,880	11.31
1400	5475	7.69	3000	14,115	11.74

Mo (g) :

 $H_T - H_{298.15} = 4.97T - 1482$ (0.1 percent; 298-1800°K)

 $H_T - H_{298.15} = 3.56T + 0.40 \times 10^{-3}T^2 - 230$ (0.2 percent; 1800-3000°K)

 $C_p = 3.56 + 0.80 \times 10^{-3}T$
 $H_T - H_{298.15} = 5.48T + 0.65 \times 10^{-3}T^2 - 1692$ ($\pm$ 1 percent; 298-1800°K)

 $C_p = 5.48 + 1.30 \times 10^{-3}T$

4

Melting Point, °C:

2620 $\pm$ 10

Heat of Fusion, cal./mole at 2890°K:

6.6 $\pm$ 0.7

Boiling Point, °C:

4800
4825

1A, 27, 31A

97, 31A

1A
31A

Considerably higher values are also given.

See Vapor Pressure

Heat of Vaporization, Kcal./mole :

128.42
117.4
121.0 $\pm$ 9.0

3fA
94
97

Transition Point, °K:

2883

1A

Heat of Transition, Kcal./mole :

5.8

1A

Heat of Sublimation, Kcal./mole at 298° K:

157.5

5

Heat Content or Enthalpy, cal./mole at 298°K : (solid) 1092

5

See Tables a and b

Heat Capacity, cal./deg./mole :

(solid) 5.61 (liquid) 10.00
6.29
(gas) 4.968 at 25°

31A
5, 31A

See Tables a and b

Molybdenum, Mo (page 3)

Decomposition Temperature :	oxidized to MoO_3 at red heat	29
Decomposition Products :	—	
Vapor Pressure :		
Press. atm.	3.9×10^{-10} 1.7×10^{-5} 8.6×10^{-4} 1.8×10^{-1} 1.0	94
Temp. °C	1727 2610 3227 4727 5560	
$\log P_{\text{mm.}} = -31,060T^{-1} - 0.2 \log T$ 9.41 (bet. 298°K and M.P.)		97
1 mm. at 3102°C		12
See also Refs. 64V1 and 66A		
X-Ray Crystallographic Data :		
System cubic	Space Group O_h	Addnl. Ref. 1 49A
	a 3.1403 at 20° 3.1468 at 25°	
	Molecules/Unit Cell 2	
Hygroscopicity :	—	
Solubility Data :	Not attacked by water, dilute acids, or concd. HCl. Practically insol. in alkali hydroxides or fused alkalies. Sol. in hot concd. HNO_3 , hot concd. H_2SO_4 , in fused KClO_3 or KNO_3 .	29, 1A
Ref. 94 gives some corrosion data in several acids.		
Health Hazard :	probably slight •	12
M.A.C., mg./m. ³ :	15	12
Safety Classifications :		
OSM:	not listed	
ICC:	not listed	
Fire and Explosion Hazard :	moderate	12, 96
Dust may react explosively with air. Sub-200 mesh dust has little or no explosive hazard. In fighting fire use powdered graphite, dolomite, sodium chloride, etc., not water.		
Heat of Combustion, cal./g. :	1810	49A
Electrostatic Sensitivity :	—	
Use in Pyrotechnics :	as a fuel	
Additional References :		
1) "Molybdenum," L. Northcott, Academic Press, Inc., New York (1956)		
2) Ref. 49A		
3) Ref. 64V1		

MOLYBDENUM TRIOXIDE, MoO_3 (Molybdic Anhydride, Molybdite)			Refs.
Percent Oxygen:	33.34		
Specification No.:	not listed		
Molecular Weight:	143.95		
Crystalline Form:	rhombic		1A
Color:	white to yellowish or colorless		1A
Density, g./ml.:	(solid) 4.50 at 19.5°C 4.692 at 21°C		1A 29
Coefficient of Thermal Expansion, cubic:	21-78°C 7×10^{-5} 78-195°C 5×10^{-5} 195-273°C 3×10^{-5}		44853
Heat of Formation, Kcal./mole at 298°K:	(c) -180.33 -178.2 ± 1.5		1A, 9 97
Free Energy of Formation, Kcal./mole at 298°K:	(c) -161.95		1A, 9
a. HEAT AND FREE ENERGY OF FORMATION OF MoO_3 (c, 1)			4
$T, ^\circ\text{K}$	ΔH (cal./mole)	ΔF° (cal./mole)	
298.16	-180,300 (± 1500)	-162,000 (± 1600)	
400	-180,100	-155,700	
500	-179,700	-149,600	
600	-179,200	-143,700	
700	-178,700	-137,800	
800	-178,200	-132,000	
900	-177,600	-126,200	
1000	-177,000	-120,600	
1068	-176,600	-116,700	
1068	-164,600	-116,700	
1100	-164,200	-115,200	
1200	-163,000	-110,800	
1300	-161,800	-106,500	
1400	-160,600	-102,300	
1500	-159,500	-98,200	
Free Energy Equations:			
<i>Reaction</i>	<i>Range of Validity, °K</i>		
1) $\text{Mo (c)} + 3/2 \text{O}_2 \text{ (g)} = \text{MoO}_3 \text{ (c)}$	298.16-1068		2
$\Delta F^\circ = -182,650 - 8.86T \log T - 1.55 \times 10^{-3}T^2 + 1.54 \times 10^5T^{-1} + 90.07T$			
2) $\text{Mo (c)} + 3/2 \text{O}_2 \text{ (g)} = \text{MoO}_3 \text{ (l)}$	1068-1500		
$\Delta F^\circ = -179,770 - 36.341 \log T + 1.40 \times 10^{-3}T^2 - 0.30 \times 10^5T^{-1} + 167.61T$			
Entropy, cal./deg./mole at 298°K:	18.68		1A, 9

Molybdenum Trioxide, MoO₃ (page 2)b. HEAT CONTENT AND ENTROPY OF MoO₃ (c, l)

4

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	1935	5.56	1068 (c) . . .	17,670	28.26
500	4035	10.24	1068 (l) . . .	30,170	39.96
600	6260	14.30	1100	31,200	40.92
700	8570	17.86	1200	34,400	43.70
800	10,940	21.02	1300	37,600	46.26
900	13,390	23.91	1400	40,800	48.63
1000	15,920	26.57	1500	44,000	50.84

MoO₃ (c) :

$$H_T - H_{298.15} = 20.73T + 2.59 \times 10^{-3}T^2 + 4.18 \times 10^5T^{-1} - 7813 \text{ (0.1 percent ; 298-1068°K)}$$

$$C_p = 20.73 + 5.18 \times 10^{-3}T - 4.18 \times 10^5T^{-2}$$

MoO₃ (l) :

$$H_T - H_{298.15} = 32.00T - 4000 \text{ (0.1 percent ; 1068-1500°K)}$$

Melting Point, °C:

795

797

PA. 24A

Addnl. Ref. 2

Melts to a dark yellow liquid, which solidifies to a yellowish-white crystalline mass.

Heat of Fusion, Kcal./mole :

11.91

12.54

2

6

Boiling Point, °K:

1530 ± 50

6, 8

The following values are also given :

1100°C

1428°K

24A

41

Heat of Vaporization, Kcal./mole :

33

9,411

Temperature of Sublimation, °K :

(gas) 973

volatile above 500°C
sublimes about 700°C

52

94

Heat of Sublimation, Kcal./mole at 691°C :

65

68.1

9, 41

Addnl. Ref. 3

Heat Content or Enthalpy:

See Table b

Heat Capacity, cal./deg./mole :

(liquid) 32.0

2

See Table b

Decomposition Temperature :

—

For DTA see Ref. 33

Decomposition Products :

—

Molybdenum Trioxide, MoO₃ (page 3)

Vapor Pressure:

Press. mm.	.009	0.05	0.30	1.75	10.1	23.4	105.1	288.3	476.2	760	44S53
Temp. °C	610	650	700	760	800	850	950	1050	1100	1155	

298°K to M.P.: $\log p_{\text{mm.}} = -15,230 - 4.02 \log T + 27.16$

24A

M.P. to B.P.: $\log p_{\text{mm.}} = 12,480T^{-1} - 4.02 \log T + 24.60$

24A

X-Ray Crystallographic Data:

<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>Molecules/Unit Cell</i>	
cubic	V_h^6	3.14103 at 25°	4	18, 44S53

Hygroscopicity:

Solubility Data:

In water, g./100 ml. at 18°C: 0.1066 1A

at 70°C: 2.065

In acids, NH₄OH, alkalies, sulfur: soluble

In acids after strong ignition: very slightly soluble 29

Health Hazard:

probably slight 12

L.D., g./kg.: 400 29

Safety Classifications:

OSM: not listed

ICC: not listed

Fire and Explosion Hazard:

Electrostatic Sensitivity:

Use in Pyrotechnics: Product of the burning of Mo and some of its compounds.

Additional References:

- 1 Ref. 7
- 2) C.A. 58, 20992 (1959)
- 3) C.A. 48, 13396 (1954)

NICKEL, Ni			Refs.		
Specification No. :	JAN-N-412A				
The standard A.S.T.M. grades of virgin nickel are :					
Electrolytic	99.5% Ni		16		
X shot	98.9% Ni				
A shot	97.75% Ni				
Ingot	98.5% Ni				
Molecular Weight :	58.71				
Crystalline Form :	cubic		1		
Color :	silvery metal		1		
Density, g./ml. :	(solid) 8.90		1		
Coefficient of Thermal Expansion, 16–250°C :	13.97 × 10 ⁻⁶		1		
Temperature °C	Coeff.				
-19 to + 16	10.12 × 10 ⁻⁶				
40	12.79 × 10 ⁻⁶				
375–1000	13.46 × 10 ⁻⁶				
25–100	12.9 × 10 ⁻⁶				
Heat of Formation, Kcal./mole at 298°K :	(gas) -101.260		5		
Free Energy of Formation, Kcal./mole at 298°K :	(gas) -90.413				
Entropy, cal./deg./mole at 298°K :	(gas) 43.52		5		
	(solid) 7.14		5		
See Tables a and b					
Melting Point:	1728°K (1455°C)		1		
Heat of Fusion, cal./mole :	4210		4, 5		
Boiling Point:	3110°K (2837°C)		5		
Heat of Vaporization, cal./mole :	88,870		5		
Transition Point :	α to β at 633°K (360°C)		4		
Heat of Transition, cal./mole :	α to β, 0		4		
Heat of Sublimation, cal./mole at 298°K:	101,260		5		
Heat Content or Enthalpy, cal./mole :	(solid) 1144		5		
	(gas) 1631				
See Tables a and b					
a. HEAT CONTENT AND ENTROPY OF Ni (c, 1)			4		
(Base, crystals at 298.15°K)					
T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	665	1.91	900	4445	8.03
500	1380	3.51	1000	5210	8.84
600	2180	4.96	1100	5985	9.58
633 (α) . . .	2460	5.42	1200	6780	10.27
633 (β) . . .	2460	5.42	1300	7600	10.93
700	2940	6.14	1400	8450	11.56
830	3690	7.14	1500	9320	12.16

Nickel, Ni (page 2)

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
1600	10,210	12.73	2200	19,910	18.0%
1700	11,110	13.28	2400	21,750	~~18.88~~
1725 (β) . . .	11,330	13.40	2600	23,590	19.62
1725 (1) . . .	15,540	15.84	2800	25,430	20.30
1800	16,230	16.24	3000	27,270	20.95
2000	18,070	17.21	3200	29,110	21.52

Ni (α) :

Enthalpy : $H_T - H_{298.15} = 4.06T + 3.52 \times 10^{-3}T^2 - 1523$ (0.3 percent ; 298-633°K)

Heat Capacity : $C_p = 4.06 + 7.04 \times 10^{-3}T$

Ni (β) :

Enthalpy : $H_T - H_{298.15} = 6.00T + 0.90 \times 10^{-3}T^2 - 1701$ (0.2 percent ; 633-1725°K)

Heat Capacity : $C_p = 6.00 + 1.80 \times 10^{-3}T$

Ni (1) :

Enthalpy : $H_T - H_{298.15} = 9.20T - 330$ (0.1 percent ; 1725-3200°K)

b. HEAT CONTENT AND ENTROPY OF Ni (g)
(Base, ideal gas at 298.15°K)

4

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	575	1.66	1900	9310	10.77
500	1150	2.94	2000	9865	11.05
600	1740	4.01	2200	10,970	11.58
700	2335	4.93	2400	12,065	12.06
800	2930	5.73	2600	13,155	12.49
900	3525	6.43	2800	14,235	12.89
1000	4120	7.06	3000	15,310	13.26
1100	4715	7.62	3500	17,985	14.09
1200	5303	8.13	4000	20,665	14.80
1300	5885	8.60	4500	23,370	15.44
1400	6465	9.03	5000	26,135	16.02
1500	7040	9.43	6000	31,940	17.08
1600	7615	9.80	7000	38,305	18.06
1700	8185	10.14	8000	45,415	19.81
1800	8750	10.46			

Ni (g) :

Enthalpy : $H_T - H_{298.15} = 5.99T + 0.36 \times 10^{-3}T^2 - 1907$ (0.3 percent ; 298-1000°K)

Heat Capacity : $C_p = 5.99 + 0.36 \times 10^{-3}T$

Enthalpy : $H_T - H_{298.15} = 6.07T - 0.11 \times 10^{-3}T^2 - 4120$ (0.4 percent ; 1000-4500°K)

Heat Capacity : $C_p = 6.07 - 0.22 \times 10^{-3}T$

Nickel, Ni (page 3)

Heat Capacity, cal./deg./mole at **298°K** :
 (solid) 6.23
 (liquid) **9.20**
 (gas) 5.58

4, 5

c. HEAT CAPACITY OF Ni
 (Solid, **298-1728°K** ; liquid, **1728-3000°K**)

5

T, °K	C _p ^o (cal./deg./mole)
298	6.23
500	7.47
800	7.44
1200	8.16
1600	8.88
1700	9.06
18003000	9.20

See equations above

Decomposition Temperature : ———

Decomposition Products : ———

Vapor Pressure:

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	1810	2057	2234	2364	2603	2732	1452

1

X-Ray Crystallographic Data :

1

System	Space Group	a	c	Atoms/ Unit Cell
(α) hexagonal	D _{6h} ⁴	2.66	4.32	2
(β) cubic	O _h ⁵	3.517		4

Hygroscopicity: Nonhygroscopic. Not affected by water.

29

Solubility Data :

1, 29

In water, fused alkalis or NH₃ :

insoluble

In dilute HNO₃ :

soluble

In HCl or H₂SO₄ :

slightly soluble

Health Hazard : Exposure to nickel **may cause** dermatitis (Nickel itch) in sensitive individuals. Ingestion of large amounts (even 1-3 mg./kg. of body weight) causes nausea, vomiting, diarrhea, depression of the central nervous system, and myocardial damage. Its health hazard is, however, considered slight.

12, 25, 29

M.A.C. ,mg./m.³ :

0.5

25

Safety Classifications :

OSM :

class 2

ICC : Listed under "Explosives and **Other** Dangerous Materials." Classed as a flammable solid; red label.

Nickel, Ni (page 4)

Fire and Explosion Hazard : Ni dust is explosive and a dangerous fire hazard. It has an ignition temperature above 700°C, and burns with intense heat. When compounded with oxidizing agents the powdered metal is a dangerous fire and explosion hazard. It decomposes steam at red heat. The amount of powdered metal which may become involved in a fire should be strictly limited. Fires must not be fought with ordinary streams of water because of the danger of liberating large quantities of hydrogen gas. Fires involving small amounts of powdered Ni may be fought with fog nozzles or special extinguishing powders.

12, 14, 49

In the repair or maintenance of buildings or equipment, powder or dust should be reduced and nonsparking tools used. Store and process only in rooms or buildings adequately ventilated at the highest point.

Electrostatic Sensitivity :

not ignited by electric
sparks

49

Use in Pyrotechnics:

as a fuel

NITROCELLULOSE (12.6% N)
(Cellulose Nitrate, Pyrocellulose, Pyro, Nitro Cellulose, Nitrocotton)

Formula : $[C_6H_{10-x}O_5-x(ONO_2)x]_n$

Where x = no. of ONO_2 groups and n = degree of polymerization. For 12.6% N, $x=2.45$.

Specification No. :

JAN-N-244

The spec. lists four **grades** of which Grade A, with $12.60 \pm 0.10\%$ N, is used for pyrotechnics.

Molecular Weight : Variable, approx. 0.42 to 0.78×10^6 or $272.3 n$ (calculated from formula)

Form : Cotton-like fibrous **solid** or amorphous powder (when cut up or beaten).

Color :

white

Density, g./ml. :

(solid) about 1.66

Coefficient of Thermal Expansion, linear :

$9-16 \times 10''$

Heat of Formation, cal./g.

-617

Free Energy of Formation :

—

Entropy :

—

Melting Point: Decomposes. In a vacuum melts at approx. $473^\circ K$ ($200^\circ C$) before exploding.

Heat of Fusion:

—

Boiling Point:

decomposes

Transition Point:

—

Heat of Sublimation:

—

Heat Content or Enthalpy :

—

Heat Capacity :

—

Decomposition Temperature: See Addnl. Refs. 1, 2, 3, 4

For DTA see Ref. 33

Decomposition Products : Depend on conditions of decomposition.

Vapor Pressure :

Press. mm.	0.0	0.0
Temp. °C	25	60

X-Ray Crystallographic Data :

for cellulose trinitrate
($x=3$)

System	Space Group	a	b	c	Axial Angle	Molecules/ Unit Cell
monoclinic		13.9	25.6	9.0	$\beta = 90^\circ$	

Hygroscopicity, g. $H_2O/100$ g. N.C. :

$\frac{334.3 - 23.65 N}{31.11 - N}$ (approx.)

or more roughly 14.6-N % nitrogen
at 30° and 90% R.H. % :

3

Refs.

Addnl. Ref. 1

1

Addnl. Ref. 1

31

13

Addnl. Ref. 2

13

Addnl. Ref. 1

Addnl. Ref. 1

13

Nitrocellulose (12.6% N) (page 2)

Solubility Data: Numerous substances dissolve or more accurately disperse pyrocellulose. Among these are acetone, ether-alcohol (2:1), fatty acid esters, nitro compounds, and organic nitrates.

In water, ether, and benzene : insoluble

Safety Classifications:

OSM : Class 12 when wet with 8-30% water.

ICC: Listed under "Explosives and Other Dangerous Materials," as a high explosive when dry and as a flammable liquid when dispersed in a solvent; red label.

Fire and Explosion Hazard : Dry nitrocellulose is extremely sensitive to shock and friction, and very dangerous when ignited, even in the open, or when heated with oxidizing agents. Dry nitrocellulose burns in an instantaneous flash. Wet nitrocellulose is less hazardous. Nitrocellulose when impure is subject to spontaneous ignition. Storage of dry nitrocellulose is not permitted as it has all the hazards of a sensitive and easily ignited high explosive. It is stored wet (25-30% water) in zinc-lined boxes or metal drums. Must contain not less than 20% moisture by weight when shipped. Caution : keep away from heat and open flame.

Flash Point, closed cup, °F : 40

Impact Sensitivity, 2 kg. wt. :

Bur. of Mines Apparatus, cm. : 8 (10% point)

Sample weight, mg. : 3 (10% point)

P.A. Apparatus, in. : 5

Explosion Temperature Test :

5 second point 170°C with decomposition

Electrostatic Sensitivity : Readily accumulates static charges when dry.

Volatility at 60°C, micrograms/cm.²/hr. : 0

Oxygen Balance to CO₂, % : -35

to CO, % : 0.6

Vacuum Stability Test, 5 g. sample

Temp. °C	90	100	120
cc. 40 hrs.	0.17	1.0	
cc. 16 hrs.			11.4

200 Gram Bomb Sand Test, 0.4 g. sample

Grams sand crushed to pass a 30-mesh sieve: 45.0

Sensitivity (initiator required for complete detonation)

Lead azide: 0.10 g.

Heat of Combustion, cal./g. : 2409

Heat of Explosion, cal./g. : 855

Gas Volume on Explosion, cc./g. : 919

Second Order Transition Temperature, °C : (approx.) 66

(nitrogen content not mentioned) :

Use in Pyrotechnics: For coating compositions to reduce the penetration of moisture, and as a bonding agent.

Addnl. Ref. 1

12, 14

12

13

13

14

13

59

20

Nitrocellulose (12.6% N) (page 3)

Additional References :

- 1) "Cellulose Nitrate," F. D. Miles, Oliver and Boyd, London and Edinburgh. Interscience Publishers, Inc., New York (1955)
- 2) "The Spontaneous Ignition of Nitrocellulose," E. K. Rideal and A. J. B. Robertson, Third Symposium on Combustion and Flame and Explosion Phenomena, The Williams & Wilkins Company, Baltimore (1949)
- 3) "Cellulose and Cellulose Derivatives," E. Ott et al., Eds., Interscience Publishers, Inc., New York (1954-55)
- 4) "The Kinetics of Thermal Decomposition of Nitrocellulose," R. W. Phillips et al., J. Phy. Chem. 59,1034 (1955)

PARLON
**(Chlorinated Rubber, Tornesit, Alloprené. Parlon is trademarked
 by Hercules Powder Co.)**



Formula : Rubber chlorinated polyisoprene $[-\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2]_x$ chlorinated approximately 67% Cl by weight.

Chlorination of rubber results in a complete reaction. There is not only addition and substitution of chlorine but also cyclization along the polymer chains. The theoretical chlorine content for the completely chlorinated isoprene unit, $\text{C}_5\text{H}_6\text{Cl}_4$, is 68.5%. Parlon is marked in five viscosity types. Stabilized Parlon usually contains 1% of an epoxy compound as a stabilizer to improve resistance to heat, ultraviolet light and moisture. Sunlight causes discoloration and embrittlement in unpigmented, unstabilized films. Parlon is resistant to dampness, soaps, molds, and mildew.

Molecular Weight : Variable (high) depending on viscosity.

Crystalline Form : Coarse amorphous inelastic powder; poorly crystallized, granular powder.

Color :

white (color of film,
water-white)

Density, g./ml. :

(solid) 1.66 (also given as
1.64 and up)

Coefficient of Thermal Expansion :

$12-13 \times 10^{-5}$

Heat of Formation :

—

Free Energy of Formation :

—

Entropy :

—

Melting Point, softening point of film :

413°K (140°C)

Heat of Fusion :

—

Boiling Point :

—

Transition Point :

—

Heat of Sublimation :

—

Heat Content or Enthalpy :

—

Heat Capacity :

—

Decomposition Temperature :

Effect of dry heat on film (continuous exposure) stable up to 125°C. Appreciable decomposition at 135°C.

Decomposition Products :

—

Vapor Pressure :

—

X-Ray Crystallographic Data :

—

Hygroscopticity : Moisture content as shipped is less than 0.5%.

Absorbs little moisture on storage.

Moisture absorption at 80% R.H. in 24 hr., % : 0.14

Water vapor transfer of free film, g./100 sq. in./mil. in 24 hr. at 95°F and 100% R.H. : 1.0

Refs.

59

Addnl. Ref. 1

59, 60, Addnl.
Refs. 1, 2

69, Addnl.
Ref. 1

Addnl. Ref. 1
60

Addnl. Ref. 1

Addnl. Ref. 1

Addnl. Ref. 1

Parlon (page 2)

Solubility Data : Soluble in CCl₄, esters, aromatic hydrocarbons, and ketones. Unaffected by strong or weak acids or alkalies, salt spray, aliphatic alcohols, and aliphatic hydrocarbons. Insoluble in acetone alone,

59, 60, Adanl.
Ref. 1

Health Hazard: nontoxic

Safety Classifications :

OSM : not listed

ICC : not listed

Fire and Explosion Hazard : Nonflammable. Will ignite in the flame of a bunsen burner, but the flame is selfextinguishing. On burning, it melts, gives off bubbles of gas and chars.

59, 60

Electrostatic Sensitivity : —

Use in Pyrotechnics: As a color intensifier and binder. Used in rapid drying paints.

59, 60, Addnl.
Ref. 1

Additional References :

- 1) "Parlon, Properties and Uses," Hercules Powder Co., Inc., Wilmington, Del. (1957)
- 2) "Rubber, Polyisoprenes, and Allied Compounds. Part IV. The Relative Tendencies towards Substitutive and Additive Reaction during Chlorination," G. F. Bloomfield, J. Chem. Soc. 1943, 289

PHOSPHORUS, P₄ (yellow), P (red)

Refs.

Specification No. : yellow, P₄
stabilized red, P

JAN-P-211
JAN-P-670

The spec. covers **two** grades, **A** and **B**, which differ in purity and granulation.

Molecular Weight:

(yellow, P₄) **123.90**
(red, P) **30.974**

4, 5

Crystalline Form and Color: The yellow or white is cubic in form; the red or reddish brown, cubic or triclinic in form; the violet, monoclinic.

1, 5

Phosphorus occurs in four allotropic forms: yellow or white, red, black, and violet. Yellow (white) phosphorus varies in color from almost colorless to pale yellow. It is a waxlike solid which phosphoresces in the dark with a greenish light and gives off white fumes. It ignites spontaneously in air. Phosphorus is produced directly from phosphate rock in the electric furnace. When distilled at **290°C**, the red modification yields white phosphorus. At 600–800°K, liquid white phosphorus is rapidly converted to red phosphorus; at 704–3000°K, the gas is mainly in the diatomic form; below 704° it is in the tetratomic form. Black phosphorus resembles graphite in texture. It is produced from white phosphorus under high pressure. Phosphorus, Ked, Spec. No. 51 P, 37, and Phosphorus, Red, stabilized, Spec. JAN-P-670 are the two types of red phosphorus used in pyrotechnics compositions. Red phosphorus is a reddish-brown powder. Stabilized red phosphorus is less sensitive and hence slightly less of a fire hazard.

1, 5, 16, 29,
Addnl. Ref. 1

Density, g./ml.:

(solid) yellow, **1.82**
red, **2.20**
black, **2.70**

1

Coefficient of Thermal Expansion, linear, 0–44°C:

124×10^{-6}

1

Heat of Formation, Kcal./mole at 298°K:

(gas) **75.18**

9

Free Energy of Formation, Kcal./mole at 298°K:

(gas) **66.71**
white (c) 0.000
red (c) **-4.4**
black (c) **-10.3**

9

Entropy, cal./deg./mole at 298°K:

white (c) **10.6**
red (c) **5.46**

9

See Tables a to e

Melting Point:

white (a) **317.4°K**
(**44.3°C**)
red, **870°K (597°C)**

5

Heat of Fusion, cal./mole:

white, **150**

5

Boiling Point:

white, **554°K (218°C)**
red, **280°K (7°C)**
(ignites in air)

1, 5

Phosphorus, P₄ (yellow), P (red) (page 2)

Transition Points and Heats of Transition :

Form		Temp. of Transition	Heat of Transition
Initial	Final	°K	Kcal./mole
c, IV	c, III	30.31	0.0197
c, III	c, II	49.44	0.186
c, II	c, I	88.12	0.116

I = black, II = red, III and IV = white

(β-white transforms to α-white at -76.9°C)

Heat of Sublimation, cal./mole at 298°K :

(white to P₄ gas) 14,100
 (red to P₄ gas) 30,820
 (P₂ gas) 42,725
 (P gas) 79,800

Addnl. Ref. 2

5

a. HEAT CONTENT AND ENTROPY OF P (red)

(Base, crystals at 298.15°K)

4

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	620	1.79	700	2690	5.62
500	1270	3.24	800	3440	6.62
600	1970	4.51			

b. HEAT CONTENT AND ENTROPY OF P₄ (white, 1)

(Base, crystals at 298.15°K)

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
317.4 (c) . .	434	1.41	370	2270	6.90
317.4 (l) . .	1034	3.30	400	2975	8.74
350	1800	5.60			

P₄ (white) :

Enthalpy : H_T - H_{298.15} = 22.501' - 6708 (0.1percent ; 298-317.4°K)

Heat Capacity : C_p = 22.50 ; A H_{317.4} (fusion) = 600

P₄ (l) :

Enthalpy : H_T - H_{298.15} = 23.50T - 6425 (0.1percent ; 314.7-400°K)

Heat Capacity : C_p = 23.50

c. HEAT CONTENT AND ENTROPY OF P (g)
(Base, ideal gas at 298.15°K)

4

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	505	1.46	1900	7975	9.21
500	1005	2.67	2000	8480	9.47
600	1500	3.48	2200	9500	9.96
700	1995	4.24	2400	10,535	10.41
800	2495	4.90	2600	11,590	10.83
900	2990	5.49	2800	12,670	11.23
1000	3490	6.01	3000	13,780	11.61
1100	3985	6.49	3500	16,685	12.51
1200	4480	6.92	4000	19,790	13.34
1300	4980	7.32	4500	23,070	14.11
1400	5445	7.69	5000	26,495	14.83
1500	5975	8.03	6000	33,605	16.13
1600	6470	8.35	7000	40,825	17.24
1700	6970	8.65	8000	47,980	18.20
1800	7475	8.94			

P (g) :

Enthalpy: $H_T - H_{298.15} = 4.97T - 1.482$ (0.1 percent ; 298-2000°K)

d. HEAT CONTENT AND ENTROPY OF P₂ (g)
(Base, ideal gas at 298.15°K)

4

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	800	2.31	1000	5910	10.06
500	1620	4.14	1200	7660	11.65
600	2450	5.65	1400	9430	13.02
		6.96			
		8.11			

P₂ (g) :Enthalpy: $H_T - H_{298.15} = 8.31T + 0.23 \times 10^{-3}T^2 + 0.72 \times 10^{-5}T^{-1} - 2740$
(0.4 percent ; 298-2000°K)Heat Capacity: $C_p = 8.31 + 0.46 \times 10^{-3}T - 0.72 \times 10^{-5}T^{-2}$

Phosphorus, P₄ (yellow), P (red) (p₂₅ 13)

4

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	1710	4.93	1300	18,900	27.21
500	3500	8.92	1400	20,860	28.67
600	5360	12.31	1500	22,830	30.03
700	7240	15.21	1600	24,800	31.30
800	9150	17.76	1700	26,770	32.50
900	11,080	20.03	1800	28,740	33.62
1000	13,020	22.07	1900	30,720	34.69
1100	14,980	23.94	2000	32,690	35.70
1200	16,940	25.65			

P₄ (g) :

Enthalpy : $H_T - H_{298.15} = 18.93T + 0.43 \times 10^{-5}T^2 + 2.81 \times 10^{-8}T^3 - 6625$
(0.2 percent; 298-1500°K)

Heat Capacity : $C_p = 18.93 + 0.86 \times 10^{-5}T - 2.81 \times 10^{-8}T^2$

Heat Capacity, cal./deg./mole at 298°K : (gas) 4.96

See tables above

Vapor Pressure :

Press. mm.	1	10	40	100	400	760	M.P.
Temp °C (yellow)	76.6	128.0	166.7	197.3	251.0	280.1	44.1
(black)	290	338	371	393	432	453	
(violet)	237	287	323	349	391	417	590

X-Ray Crystallographic Data:

System	Space Group	a	b	c	Unit Cell Molecules/
red, black (rhombic)	V ₁₈	3.31	4.38	10.50	8
(yellow) (cubic) (at 35°C)		7.17			16 (4P₄)

(Crystalline and amorphous black and red P give similar X-ray patterns)

Hygroscopicity, Red P at 70°F and 216 hr. exposure:

R.H.	50	76	90
Gain in wt. %	2.04	5.0	11.06

Solubility Data :

Yellow or White	Red
H ₂ O : 0.0003 g./ml. at 15°C slight in hot	very slight insol. in hot water
Alcohol : 0.3 g./100 ml.	slight in abs. alc.
CS ₂ 880 g./100 ml. at 10°C	insol. in CS ₂ , ether, NH ₃

Phosphorus, P₄ (yellow), P (red) (page 5)

Benzene : 1 g. in 35 ml.	
CHCl ₃ : 1 g./ 10 ml.	
Oilve oil: 1 g./ 80 ml.	
Oil of Turpentine : 1g./60 ml.	
Sl. sol. in NH ₃ , alkalies, ether	
Health Hazard: Yellow phosphorus is poisonous even when ingested in small amounts. An approximate fatal dose is 50 mg. Phosphorus fumes are also very poisonous. External contact may cause severe burns. Long continued absorption can cause necrosis of the jaw bone and chronic poisoning. Phosphorus is especially dangerous to the eyes.	12, 29
M.A.C. (yellow phosphorus), mg./m. ³ :	0.1
	14
Red phosphorus is poisonous on inhalation or ingestion but slower acting than yellow phosphorus. It should never be allowed to come in contact with the eyes.	12, 93
Phosphorus poisoning is detectable in the urine.	12
Safety Classifications :	
OSM : Class not specified. As a fire hazard it should be listed in class 1.	
ICC : Flammable solid ;yellow label.	
U.N. Phosphorus, white or yellow, dry, or under water, or in solution is classified as an inflammable solid, liable to spontaneous combustion.	
Fire and Explosion Hazard : On exposure to air white phosphorus (WP) bursts into flame and is thus a serious fire hazard. Containers or ammunition containing WP should be kept below its M.P. or 44.1°C, as pressure may rupture the container. Phosphorus is preferably stored under water in sealed metal vessels enclosed in wooden boxes or metal drums, WP is dangerous when heated with oxidizing agents, as it emits highly toxic fumes of oxides of phosphorus. Use water to fight fire. Red phosphorus, while less reactive than yellow phosphorus, is a dangerous fire hazard. It is easily ignited by spark or friction and is dangerous when in contact with organic materials or oxidizers. It can ignite spontaneously in air. It emits highly toxic fumes when heated.	12, 14
Autoignition Temperature, in air, °F :	(yellow) 86
	(red, amor.) \$00
	75, 29
	67, 71
Use in Pyrotechnics : As a fuel, in incendiary and smoke compositions.	
Additional References :	
1) "Two New Modifications of Phosphorus," P. W. Bridgman, J. Am. Chem. Soc. 36, 1334 (1914)	
2) "Phosphorus and Its Compounds," Vol. I, J. R. Van Wazer, Interscience Publishers, Inc., New York (1958)	

PLURONIC F 68

Following information comes from the Wyandotte Chemicals Corporation, Wyandotte, Michigan, manufacturers of Pluronic F 68.

Pluronic F 68 is a block-polymer prepared by adding propylene oxide to the two hydroxyl groups of a propylene glycol nucleus. The resulting hydrophobic base can be made to any desired length, varying from 800 to many thousands in molecular weight. By adding ethylene oxide to this hydrophobic base, it is possible to put polyoxyethylene hydrophilic groups on the end of the molecule. These hydrophilic groups can be controlled in length to constitute anywhere from 10 to 90% of the final molecule. The simplified structure can be represented as $\text{HO}(\text{CH}_2\text{-CH}_2\text{-O})_n(\text{CH}_2\text{-CH}_2\text{O})_m(\text{CH}_2\text{-CH}_2\text{O})_n\text{H}$.



Pluronic F 68 is a flake with a hydrophobic base molecular weight of approximately 1750; 80% of the molecule, by weight, consists of hydrophilic polyoxyethylene groups and the remaining 20% hydrophobic polyoxypropylene groups. The total molecular weight of F 68 = $1750 \times 1.20 = 8750$.

pH of 2.5% aqueous solution :

.20
7

Cloud Point:

of aqueous solutions in concentrations up to 60.0% :

at 10% concentration:	> 100°C semi-solid
of 10% aqueous solutions at pH 2 and 10	
in 4% NaOH:	> 100°C
40 % concentration:	semi-solid
20% concentration :	26.5°C
100% concentration :	38.5°C
1% concentration :	47°C

Solubility in Organic Solvents at 25°C in g./100 ml. solvent:

Samples of 0.1, 1.0, 5.0, and 10.0 g. were dissolved in 100 ml. of solvent and observed after 30 min. for any phase separations, turbidity, etc.

Ethyl alcohol (95%) :	> 10.0
Toluene:	5.0
Perchloroethylene :	insol.
Kerosene:	insol.
Ethylene glycol :	insol.
Vegetable oil :	insol.
Mineral oil:	insol.

Surface Tension at 25°C, dynes/cm.:

1.0% solution	41.9
0.1% solution	45.6
0.01% solution	49.9
0.001% solution	53.3

Using a DuNuoy Tensiometer, samples are in aqueous solutions at the specified concentrations.

Concentration Required for a 25 sec. Draves Sink Time:

At both 25° and 50°C, the maximum concentration evaluated was 5 g./l. At this concentration the sink time was 300 seconds.

Use in Pyrotechnics: A surface acting agent used as a detergent, emulsifier, and wetting agent.

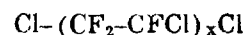
POLYCHLOROTRIFLUOROETHYLENE (Kel-F Brand Oils and Waxes)

Refs.

KEL-F oils and waxes are low molecular weight polymers of chlorotrifluoroethylene ($\text{CF}_2 = \text{CFCl}$) which constitute a homologous series of compounds composed of chlorotrifluoroethylene repeating units and terminal chlorine atoms. This series is referred to as "whole telomer." KEL-F oils and waxes are made by Minnesota Mining and Manufacturing Co.

All data from
Addnl.
Ref. 1

Formula :



Specification No. :

MIL-M-55028A

Molecular Weight: From 303 for the lowest boiling (dimeric) component of #1 oil to 5-10,000 for the highest melting ingredients of #200 wax.

Color: All **KEL-F** oils and waxes are colorless and odorless. In the liquid state all products are clear and free from sediment. At room temperature the oils are transparent, and the waxes take on a translucent or opaque white appearance.

Specific Gravity: KEL-F oils are comparatively dense, with values approaching twice the density of water. The waxes are generally greater than twice the density of water at temperatures less than 25°C. Specific gravity depends less markedly on temperature than does viscosity.

Vapor Pressure: Because of their low heats of vaporization and **weak** intermolecular forces, the oils and waxes are characterized by relatively high vapor pressures. Values can be calculated by means of the vapor pressure constants and equation in the table of typical properties. (See below).

Solubility: The oils and waxes are soluble in aromatic, aliphatic, and chlorinated hydrocarbons, alcohols, ketones, esters and fluorocarbons; and insoluble in water and mineral acids. The degree of solubility varies widely with molecular weight; the waxes are less soluble than the oils.

Viscosity: KEL-F oils are available in three viscosity grades (1, 3, 10 centistokes at 210°F). #40 wax, by virtue of its low melting point, can also be considered as an extra-heavy oil (viscosity = 40 cs. at 210°F). Viscosities of halofluorocarbon liquids depend markedly on temperature.

TYPICAL PROPERTIES OF STANDARD KEL-F OILS AND WAXES

	Grade Designation					
	1	3	10	40	10-200	200
Molecular Weight	500	630	780	940	—	—
Clarity (R.T.)	clear	clear	clear	opaque	opaque	opaque
Refractive Index, n_D						
77°F	1.400	1.405	1.410	—	—	—
160°F	—	—	—	1.398	1.401	—
Viscosity, centipoises						
100°F	2	25	220	—	—	—
210°F	0.8	3	10	40	55	—
266°F	—	—	—	—	—	145
Viscosity, centipoises						
160°F	3.6	47	425	—	—	—
210°F	—	5	18	75	105	—

	Grade Designation					
	1	3	10	40	10-200	200
Viscosity, Temp. Coeff. ¹	0.67	0.88	0.96	—	—	—
Pour Point, °F	< -70	-45	+30	+90	—	—
Melting Point, ASTM, D-127°F	—	—	—	100	150	200
Specific Gravity						
68°F/39°F	1.84	1.93	1.96	—	2.02	2.11
100°F/39°F	1.81	1.90	1.93	—	1.99	—
160°F/39°F	—	1.85	1.88	1.92	1.94	—
Vapor Pressure Constants ²						
A	7.4991	8.4976	9.0503	10.2123	9.6116	—
B	2351	3161	3743	4863	4313	—
Heat of Vaporization						
cal./g.	21	23	22	23	—	—
Kcal./mole	10.7	14.5	17.1	22	—	—
Surface Tension, dynes/cm.	23	28	30	—	—	—
Specific Heat, cal./g.	—	—	0.22	—	—	—
Thermal Conductivity						
BTU/hr./ft. ² /°F/ft.	—	—	0.080	0.110	—	—
Heat of Formation, cal./g. ³	-1200	-1200	-1200	-1200	-1200	-1200

¹ V.T. Coeff. = 1-Vis at 210°F/Vis at 100°F

² log P (mm. Hg) = A-B/T°K

³ calculated

Dielectric Properties: The oils and waxes have very good electrical properties. The dielectric strength of KEL-F oil (0.100 in. gap) is 500 volts/mil. The volume resistivity is in excess of 10¹⁴ ohm-cm.

Corrosivity: The oils and waxes are noncorrosive, in themselves, towards metals. Storage in nickel, monel, mild steel, stainless steel, and even aluminum offers no problems under ambient conditions. However, the oils are not rust-inhibiting, and therefore moisture should be excluded from containers.

Chemical Stability: KEL-F oils and waxes are extremely stable against the attack of strong acids, alkalis, and oxidants. No reaction has been observed with permanganate, chromic acid, fuming nitric acid, or hydrogen peroxide. The oils are not attacked by ClF₃ at 300°F, concentrated H₂SO₄ at 400°F, or concentrated aqueous alkali at the boiling point. Oxygen and ozone do not react appreciably with KEL-F oils; indeed there is evidence that the oils are even more chemically stable in the presence of oxygen. Under stringent oxidizing conditions (2000 psig. O₂ at 300°F for 8 hr.) tests have shown no change in KEL-F oil alone or in contact with a variety of metals. Nor is there any effect on the metals themselves, including copper. *Caution: Softer metals such as aluminum and magnesium may react vigorously with KEL-F oils under conditions of high shear, where fine particles of fresh metal are exposed.*

Health Hazard: The oils and waxes are substantially nontoxic and physiologically inert. However, thermal decomposition products at extremely elevated temperatures (600°F) are toxic and adequate ventilation under these conditions is strongly recommended.

Polychlorotrifluoroethylene (page 3)

Fire and Explosion Hazard : Because of their high fluorine and chlorine content, the KEL-F oils and waxes do not support combustion—that is, they are selfextinguishing once the igniting source is removed.

Infrared Transmission : As halofluorocarbons are substantially free of hydrogen, the KEL-F oils and waxes are transparent in the 2-4 micron infrared region, where most organic liquids are strongly absorbing.

Use in Pyrotechnics : Oxidizing agent in pyrotechnic compositions.

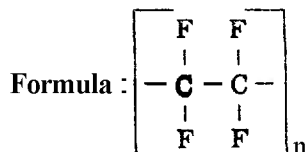
Additional References :

- 1) "KEPF Brand Halofluorocarbon Oils, Waxes, Greases and Alkanes," Minnesota Mining and Manufacturing Company (1958)

POLYTETRAFLUOROETHYLENE

(Teflon, Fluon, Fluoroflex, Polytetrafluoroethylene Resin)

Teflon is a thermoplastic, homopolymer composed of long chains of $-CF_2-$ units. Its useful temperature range is -75° to $+250^\circ C$. It cannot be molded, but at $205^\circ C$ it can be extruded. It is not wetted or affected by water, neither does it stick to anything. Teflon is the term used in the U.S. and Fluon in Great Britain.



Where n is unknown (see Molecular Weight).

Specification No. :

PA-PD-614

Covers one type of general purpose molding or extruding material and the quality of the final molded or extruded parts. The applicable A.S.T.M. Specifications and Test Methods are D1457, D257, D150, D638, D785, D256, D792, D648, D696, D543, D542.

Molecular Weight : Unknown ; estimated at 500,000 or more and possibly many millions.

Form and Color : Colorless to grey powder, flakes, or grains. Transparent in thin sheet. Teflon is highly crystalline with no appreciable cross linking. A degree of crystallinity of 93-97% has been calculated for the polymer with a density of 2.296. Teflon is available as film, laminations, powder (pellets or granules), rods or tubes (extruded), or sheets. It is fabricated by extrusion, hoe forming or drawing, compression molding, and injection molding.

Density, g./ml.:

(solid) 2.1-2.3

Coefficient of Thermal Expansion, linear :

5.5×10^{-5}

Below 15° and above $25^\circ C$ the cubical coefficients of expansion are roughly of the same order, 3×10^{-4} cc./cc./ $^\circ C$, but at about $20^\circ C$ there is a 1% increase in volume, presumably due to a change in crystal structure.

Heat of Formation, Kcal./monomole at $298^\circ K$:

(estimated for particular sample used)

-193.5

-199

Free Energy of Formation:

Entropy, Enthalpy, and Heat Capacity :

Form	Temp. $^\circ C$	Entropy abs.j. $^\circ K^{-1} g^{-1}$	Enthalpy abs.j. g^{-1}	Heat Capacity* abs.j. $^\circ K^{-1} g^{-1}$
powder	280	1.005	140.5	1.036
	310	1.134	178.6	0.9959
molded	280	1.019	144.6	1.012
	310	1.137	179.3	1.021
annealed	280	1.011	142.9	0.9761
	310	1.135	179.4	1.023

*Experimental data show that the heat capacity of a Teflon sample varies with its mechanical and thermal history.

Refs

29, 60

29

1

40, 68

68, 1

1

1, 10,
Addnl.

Ref. 12

Addnl.

Ref. 10

Addnl.

Ref. 7

Addnl. Refs.

14, 15

Addnl. Ref.

11

Polytetrafluoroethylene (page 2)

Melting Point:	(softening) 600°K (327 ± 5°C)	Spec., 68	
Heat of Fusion:	—		
Boiling Point :	above 673°K (400°C)	40	
Teflon begins to evaporate without melting.			
Heat of Polymerization, Kcal./mole of monomer :	-47	Addnl. Ref. 14	
Transition Point and Phase Changes:		68	
Teflon crystallizes in two forms. A first order phase change occurs at about 292°K (19°C) and melts at 600°K (327°C). A second order transition, involving the crystalline phase, occurs at about 303°K (30°C). This is not related to the glass transition which has not been located in this polymer, but it must be below 173°K (-100°C) as the polymer is still flexible at this temperature.			
Heat of Sublimation :	—	Addnl. Ref. 3, 9, 10, 11, 12, 13	
COMPARISON OF THE ENTHALPY AND ENTROPY CHANGE IN THE INTERVAL 280-310°K			
Sample and run	AH	AS	
Teflon powder :	abs.j.g ⁻¹	abs.j°K ⁻¹ g ⁻¹	Addnl. Ref. 11
Run 4	38.02	0.1293	
Run 6	38.04	0.1294	
Molded Teflon:			
Run 3	34.68	0.1177	
Run 4	34.75	0.1180	
Annealed Teflon :			
Run 2	36.42	0.1236	
Run 4	36.53	0.1240	
Quenched Teflon:			
Run 2	35.49	0.1205	
Specific Heat, cal./deg./g.:	0.28		Addnl. Ref. 7
Above 40°C (powdered) :	C _p = 0.2227 + 2.50 × 10 ⁻⁴ t (°C)		Addnl. Ref. 8
(drawn)	C _p = 0.2227 + 2.39 × 10 ⁻⁴ t (°C)		
Decomposition Temperature:	about 400°C		1
Decomposition Products:			68, 70, 60,
Depolymerizes to the monomer. Above 750°F decomposition liberates F ₂ . The polymer decomposes at elevated temperatures. In a vacuum, the monomer is the chief product. At low temperatures (250-350°C) degradation seems to start at the chain ends, at higher temperatures random cleavage becomes more important. In air degradation is more complicated, giving off extremely toxic products. Teflon decomposes slowly above 525°F.			Addnl. Refs. 2, 4, 5
Vapor Pressure at 25°C, mm.:	1 × 10 ⁻⁷		Addnl. Ref. 6
in the equation log p _{mm.} = A-B/T, A = 4.3, and B = 3400 over the range 300-450°K.			

Polytetrafluoroethylene (page 3)

X-Ray Crystallographic Data :

<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>Axial Angle</i>	<i>Molecules/ Unit Cell</i>
pseudohexagonal		5.54	5.54	16.8	$\gamma = 119.5$	hightemp. form 15 low temp. form 13

The chain repeat distance is **2.62A**.

Hygroscopicity :

nonhygroscopic

Solubility Data : There is no known solvent or plasticizer for Teflon. It is unaffected by strong acids, even aqua regia, and by **strong** alkalies. However, prolonged contact with fluorine, hot plasticizers, and polymeric waxes should be avoided.

Health Hazard: Heated to decomposition it gives off **toxic fumes** of **F** and **F** compounds.

Safety Classifications :

OSM :

not listed

ICC :

not listed

Fire and Explosion Hazard :

nonflammable

Electrostatic Sensitivity :

Mechanical Properties :

Modulus of elasticity, 10^8 psi :

33-65

Tensile strength, psi :

1500-3000

Ultimate elongation, % :

120-350

Yield stress, psi :

1600-2000

Yield strain, % :

50-70

Rockwell hardness :

J 75-J 95

Notched Izod impact test:

2.5-4.0

Refractive Index :

1.585-1.600

Use in Pyrotechnics: To make inert seals or containers for pyrotechnic compositions, and as an oxidizing agent.

Additional References :

- 1) Nature **174,549 (1954)**
- 2) D. K. Harris, The Lancet, **1008 (1961)**
- 3) C. E. Weir, J. Research **NBS 50, 95 (1963)**
- 4) S. L. Madorsky et al., ibid. **51,327 (1953)**
- 5) R. E. Florin et al., ibid. **53, 121 (1954)**
- 6) "Vapor Pressure of Plastic Materials," N. Jensen, J. Appl. Phys. **27, No. 12 (1956)**
- 7) "Combustion Calorimetry of Organic Fluorine Compounds," W. Good et al., J. Phys. Chem. **60,1080 (1956)**

Polytetrafluoroethylene (page 4)

- 8) "Specific Heat of Synthetic High Polymers. V. A Study of the Order-Disorder Transition of Polytetrafluoroethylene," P. Marx and M. Dole, J. Am. Chem. Soc. 77,4771 (1955)
- 9) Structural Reports 12, 367-68 (1949)
- 10) "A Room Temperature Transition in Polytetrafluoroethylene," H. Rigby and C. W. Bunn, Nature 164, 583 (1949)
- 11) "Calorimetric Properties of Polytetrafluoroethylene (Teflon) from 0° to 365°K," G. Furukawa et al., J. Research NBS 49, 273 (1952)
- 12) C.A. 52, 15118 (1958)
- 13) C.A. 52, 12516 (1958)
- 14) "Thermal Stability of Polytetrafluoroethylene," C. R. Patrick, Nature 181, 698 (1958)
- 15) "Thermochemical Studies of Fluorocarbons," H. C. Duus, Ind. Eng. Chem. 1445 (1955)

POLYVINYLCHLORIDE, PVC		Refs.
(Exon, Geon, Koroseal, Marvinal, Pliovic, Tygon, Velou, Vinylite, Vygen, Agilide)		59, 60
Formula : Approximately $(-\text{CH}_2\cdot\text{CHCl}\cdot\text{CHCl})_n$, where $n \approx$ about 4000		59
A variable polymer. Specification calls for $56 \pm 1\%$ Cl		
Specification No. :	MIL-P-20307 (includes Army Spec. No. 50-11-147)	
Molecular Weight :	variable, approximately 250,000	59
Crystalline Form :	(spec. grade) powder	
In PVC, units of the polymer chains are arranged essentially head-to-tail. In addition there may be some branching as a result of chain transfer during polymerization. Solid PVC is only slightly crystalline.		68
Color :	colorless to amber	1
Density, g./ml. :	(solid) unplasticed 1.4	59
Specification, Apparent Density :	0.5 ± 0.1 g./ml.	Addnl. Ref. 1
Coefficient of Thermal Expansion, linear :	$5-6 \times 10^{-5}$	Addnl. Refs. 1, 8
Heat of Formation, Kcal./mole at 25°C, per monomer unit :	$22.6 \pm .3$	Addnl. Ref. 7
Free Energy of Formation :	—	
Entropy :	—	
Melting Point :	Variable, depending on degree of polymerization. Begins to soften between 343° and 353°K (70° and 80°C). High molecular weight polymers do not flow well enough for practical molding below 423°K (150°C). Second order transition temperature approx. 348°K (75°C).	59, Addnl. Refs. 8, 6
Heat of Fusion :	—	
Boiling Point :	—	
Transition Point :	see Melting Point	
Heat of Sublimation :	—	
Heat Content or Enthalpy :	—	
Heat Capacity :	—	
Decomposition Temperature :	For TGA see Addnl. Ref. 9	
Decomposition Products :	HCl and darkening	
PVC begins to break down even as low as 150°F. It is also unstable to light, darkening as HCl is evolved. Stability to both heat and light can be greatly improved by the addition of stabilizers. As the loss of HCl appears to be autocatalytic, the stabilizers used are usually mild alkalies, alkali or alkali earth oxides and hydroxides, fatty acid salts, or HCl acceptors; e.g., acetylene oxide compounds. Alcoholates, carbonates, amines and many compounds have been found to be effective stabilizers. These can be used alone or in combination to adjust the properties of the plastic in the direction desired, e.g., flexibility, improved flame resistance.		59

Polyvinylchloride, PVCl (page 2)

Vapor Pressure :

X-Ray Crystallographic Data : Partly crystalline; fiber period $5.0 \pm .05$ Å or a multiple of 5.0 Å

Hygroscopicity, Specification Grade Material : Gain in mg./g. at R.T. after exposure in static and vacuum desiccators :

Time, days	65% R.H.		75% R.H.		86% R.H.		93% R.H.	
	Stat.	Vac.	Stat.	Vac.	Stat.	Vac.	Stat.	Vac.
1	0.1	0.1	0.3	0.3	0.5	0.1	0.7	0.2
7	0.6	0.3	0.2	0.1	0.3	0.5	0.7	0.2
30			0.1		0.1		0.1	

Addnl. Ref. 3

32

59

1, 59, 60

Addnl. Ref. 7

POTASSIUM, K
(Kalium)

		<i>Refs.</i>
Specification No. :		
Molecular Weight :	39.100	
Crystalline Form :	cubic	1
Color :	silvery metal	1
Density, g./ml.:	(solid) 0.87 ^{20*}	1
Coefficient of Thermal Expansion, linear at 0-50°C:	85×10^{-6}	27
Heat of Formation, Kcal./mole at 298°K :	(monatomic gas) 21,420 (diatomic gas) 30,580	5
Free Energy of Formation, Kcal./mole at 298°K :	(monatomic gas) 14,589 (diatomic gas) 21,965	5
Entropy, cal./deg./mole at 298°K :	(monatomic gas) 38.30 (diatomic gas) 59.67 (c) 15.39	6
See tables below		
Melting Point:	336.4°K (63.3°C)	4, 5
Heat of Fusion, cal./mole :	558	
boiling Point :	1039°K (766°C)	5
		5
		5
		4, 5
		4

$T, ^\circ\text{K}$	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	$T, ^\circ\text{K}$	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
336.4 (c) . . .	286	0.90	700	3515	7.97
336.4 (l) . . .	844	2.56	800	4225	8.92
400	1330	3.89	900	4940	9.76
500	2075	5.55	1000	5665	10.53
600	2805	6.88	1100	6400	11.23

K (c) :

Enthalpy: $H_T - H_{298.15} = 1.34T + 9.70 \times 10^{-3}T^2 - 1262$ (0.1 percent; 298-336.4°K)

Heat Capacity: $C_p = 1.34 + 19.40 \times 10^{-3}T$

Potassium, K (page 2)

K (l) :

Enthalpy: $H_T - H_{298.15} = 7.06T - 0.70 \times 10^{-5}T^2 - 1323$ (0.3 percent; 336.4–1100°K)

Heat Capacity: $C_p = 7.06 + 0.70 \times 10^{-5}T^2$

b. HEAT CONTENT AND ENTROPY OF K (g)

(Base, ideal gas at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	505	1.46	1900	7965	9.21
500	1005	2.57	2000	8465	9.46
600	1500	3.48	2200	9475	9.94
700	1995	4.24	2400	10,490	10.39
800	2495	4.90	2600	11,525	10.80
900	2990	5.39	2800	12,580	11.19
1000	3490	6.01	3000	13,660	11.56
1100	3985	6.48	3500	16,540	12.45
1200	4480	6.92	4000	19,810	13.32
1300	4980	7.32	4500	23,750	14.25
1400	5475	7.69	5000	28,720	15.29
1500	5975	8.03	6000	42,950	17.87
1600	6470	8.35	7000	62,210	20.83
1700	6970	8.65	8000	82,400	23.53
1800	7465	8.94			

K (g) :

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	925	2.67	1600	12,240	15.65
500	1840	4.71	1700	13,215	16.24
600	2760	6.39	1800	14,200	16.80
700	3685	7.82	1900	15,180	17.33
800	4615	9.06	2000	16,170	17.84
900	5550	10.16	2100	17,165	18.33
1000	6490	11.15	2200	18,165	18.79
1100	7440	12.05	2300	19,170	19.24
1200	8390	12.88	2400	20,180	19.67
1300	9345	13.65	2500	21,195	20.08
1400	10,305	14.36	2750	23,760	21.06
1500	11,270	15.02	3000	26,350	21.96

Potassium, K (page 5)

$K_2(g)$:

Enthalpy : $H_T - H_{298.15} = 8.91T + 0.26 \times 10^{-3}T^2 - 2680$ (0.1 percent ; 298–3000°K)

Heat Capacity : $C_p = 8.91 + 0.52 \times 10^{-3}T$

For tables of thermodynamic values see Ref. 5

Decomposition Temperature : _____

Decomposition Products : _____

Vapor Pressure :

Press. mm.	1	10	40	100	400	760
Temp. °K	341	443	524	586	708	774

At M.P. vapor pressure is 0.23 mm.

X-Ray Crystallographic Data :

System	Space Group	a	Atoms/Unit Cell
cubic	O_h^2	5.333	2

Hygroscopicity : Reacts with water to form KOH and H_2 .

Caution : Keep under liquid containing no oxygen ; e.g., petroleum or in an inert atmosphere of argon or nitrogen.

Solubility Data : Soluble in liquid NH_3 , ethylene diamine, aniline, and mercury.

Reacts with water, and alcohol.

Health Hazard : **Extremely** caustic to all tissues. The fumes of potassium oxide are very toxic.

Safety Classifications :

OSM :

Class 2

ICC : **Listed** under “Explosives and Other Dangerous Materials” as a “Flammable Solid” ; yellow label.

Fire and Explosion Hazard: Potassium reacts vigorously with water to form caustic **KOH** and **evolve** hydrogen. The heat evolved causes the potassium to melt and the hydrogen to burn. If there is any confinement, the hydrogen **may explode**. Burning potassium is difficult to extinguish. To fight a fire, use dry powdered soda ash, graphite, or special mixtures of **dry** chemicals. Even when stored under mineral oil, the peroxide (K_2O_2) and superoxide (KO_2 or KO_4) may form, and an explosion may occur when the material is handled or cut. Potassium which has become coated with a layer of oxide should be burned. The fumes of potassium oxide are highly toxic. Do not use CCl_4 on fire as an explosion may result. Use powdered talc.

Electrostatic Sensitivity : _____

Use in Pyrotechnics : As a fuel and to color burning smoke compositions violet.

Additional Reference :

- 1) C.A. 37,2578 (1943)

1

34

I

12

14

1, 29

12,14,16,75,
Addnl. Ref. 1

POTASSIUM BICARBONATE

(Potassium Acid Carbonate,
Potassium Hydrogen Carbonate)

Refs.

Formula:	KHCO ₃	
Specification No.:	MIL-P-3173	
Molecular Weight:	100.11	
Crystalline Form:	monoclinic	1
Color:	colorless	1
Density, g./ml.:	(solid) 2.17	1
Coefficient of Thermal Expansion:	—	
Heat of Formation, Kcal./mole at 298°K:	-229.3	1, 9
Free Energy of Formation, Kcal./mole at 298°K:	-205.7	86
Entropy:	—	
Melting Point:	—	
Heat of Fusion:	—	
Boiling Point:	—	
Transition Point:	—	
Heat of Sublimation:	—	
Heat Content or Enthalpy:	—	
Heat Capacity:	—	
Decomposition Temperature, °C:	100-200	1
Decomposition Products:	K ₂ CO ₃ + CO ₂ + H ₂ O	44V22 II
Heat of Dissociation, cal./mole:	15,730	Addnl. Refs. 1, 2
Vapor Pressure of Dissociation (to CO ₂ + H ₂ O) is given by		Addnl. Ref. 1
$\log P_{mm.} = 10.832 - \frac{3420}{T_{abs.}}$		
$2KHCO_3(s) = K_2CO_3(s) + CO_2(g) + H_2O(g)$		
Press. atm.	.0054 .1463 .2527 .6203 .8034 .9645	91
Temp. °K	340.8 389.5 400.3 419.4 424.9 429.1	
X-Ray Crystallographic Data:		
Space Group	a b c Axial Angle Molecules/Unit Cell	18V4
C _{2h}	15.176 5.630 3.708 β = 103° 45' 4	
Hygroscopicity:	Nonhygroscopic. Stable in dry air. In more than 70% saturated humidity it absorbs water. In damp air loses CO ₂ and forms a coating of K ₂ CO ₃ .	44V22 II
Solubility Data:	In cold water: 22.4 g./100g. •	1
	In water at 60°C: 60 g./100g.	
	In alcohol: insoluble	
Wealth Hazard:	Excessive doses may cause hyperkalemia or alkalosis.	29

Potassium Bicarbonate (page 2)

Safety Classifications :

OSM :

not listed

ICC :

not listed

Fire and Explosion Hazard:

—

Electrostatic Sensitivity :

—

Use in Pyrotechnics: As a retardant, and to color burning compositions purplish-red.

Additional References:

- 1) "The Dissociation Pressures of the Alkali Carbonates. Part 11. Potassium, Rubidium, and Cesium Hydrogen Carbonates," R. M. Caven and H. J. Sand, J. Chem. Soc. **105,2752** (1914)

POTASSIUM CHLORATE, KClO_3

Refs.

Specification No..

MIL-P-150 A

Specification Grades and Classes : The specification covers three grades : Grade A, low bromate content; Grade B, high bromate content; and Grade C with magnesium carbonate. Grade C is divided into seven classes based on granulation. Grade A is used in primer mixtures, Grade B in pyrotechnic mixtures, and Grade C in colored smoke mixtures.

Molecular Weight : 122.55

Crystalline Form : monoclinic

Percent Oxygen : 39.17

Color : colorless

Density, g./ml. : (solid) 2.32

Coefficient of Thermal Expansion, γ , over the range

-78° to +21°C: 22×10^{-6}

Heat of Formation, Kcal./mole at 298°K : -93.50

Free Energy of Formation, Kcal./mole at 298°K : -69.29

Entropy, cal./deg./mole at 298°K : 34.17

Melting Point : 641.5°K (368.4°C)

Literature Values : 334-372°C

Heat of Fusion : —

Boiling Point : Decomposes at 673°K (400°C) giving off O.

Transition Point : Monoclinic to rhombic 528°K (255 ± 5°C)

Heat of Sublimation : —

Heat Content or Enthalpy : —

Heat Capacity, cal./deg./mole at 298°K : (solid) 23.96

Temp. °C C_p , cal./deg./mole

-150 14.7

-100 18.9

0 23.4

50 25.1

100 28.4

200 36.2

225 39.7

Decomposition Temperature : For DTA and TGA see Ref. 33

Decomposition Products : At fusion $2\text{KClO}_3 \rightarrow \text{KClO}_4 + \text{KCl} + 2\text{O}_2$

At high temperature the KClO_4 decomposes to $\text{KCl} + 2\text{O}_2$

Heat of Decomposition, kg./cal./mole :

Crystalline decomposition, R.T.

Value

$\text{KClO}_3 \rightarrow \text{KCl} + \text{O}_2$ 12.1 ± 0.3

$\text{KClO}_3 \rightarrow \text{KCl} + 3\text{O}$ -9.7

$4\text{KClO}_3 \rightarrow \text{KClO}_4 + \text{KCl}$ 63

1

4V22 I

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1, 20

12, 44V22 1

9

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20, 29

Addnl. Ref. I

Potassium Chlorate, KClO₃ (page 2)

Vapor Pressure: —

X-Ray Crystallographic Data :

<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>Axial Angle</i>	<i>Molecules/ Unit Cell.</i>
monoclinic	C _{2h} ²	4.647	5.585	7.085	$\beta = 109^\circ 33'$	2
	$^\circ C$	<i>a</i>	<i>b</i>	<i>c</i>		
	20	4.647	5.585	7.085		
	90	4.665	5.600	7.122		
	150	4.679	5.611	7.152		
	200	4.692	5.621	7.180		
	250	4.706	5.632	7.209		

Hygroscopicity: R.T., after equilibrium has been established in a vacuum desiccator :

R.H.%	65	75	86	93
Time Exposed	24 hrs. equil.	24 hrs. equil.	24 hrs. equil.	24 hrs. equil.
Gain mg./g.				
R ¹	0.1	0.1	0.1	0.2
S ¹	—	<.1	0.2	—

R¹ = reagent grade ; S¹ = spec. grade

Critical R.H.

Reagent grade, 97.7% at 25°C

Spec. grade, 97.9% at 26.2°C

Water absorbed by 2.000g. at 25°C (C.P. material) :

Fineness	Hours	g. H ₂ O absorbed
40-80 mesh	45 1/4	0.0660
	69 3/4	0.1056
	93 1/2	0.1392
	122 1/4	0.2340
ground	16	0.0248
very fine	69	0.1062
	88 3/4	0.1488

Solubility Data: In water at 20°C:
at 100°C :

7.1 g./100 ml.
57 g./100 ml.
slightly soluble

In alkalis :

At 25°C, g./100 g. solvent :

In ethyl alcohol :

0.81

In glycerol :

1.05

In acetone:

insoluble

In ethylene glycol :

1.21

At 20°C in methyl alcohol:

0.095

Potassium Chlorate, KClO_3 (page 3)

Health Hazard : Slight to moderately poisonous. The principal toxic effects of chlorates are the production of methemoglobin and the destruction of red blood corpuscles. Chlorates are also irritating to the genito-urinary tract and to the kidneys. The probable lethal human dose is 50-500 mg./kg.

12, 25, 26,
29, 65, 93

Safety Classifications :

OSM : Class 1. Class 2 when not packed or stored in original containers or equivalent.

ICC : Listed under "Explosives and Other Dangerous Articles" and classed as oxydizing material : yellow label.

Fire and Explosion Hazard : Potassium chlorate is exploded by shock, or heat, and when rubbed in the presence of organic or reducing material (sugar, charcoal, shellac, sulfur, starch, sawdust, H_2SO_4 , NH_4 compounds, cyanides, phosphorus or antimony sulphide). KClO_3 is sensitive to friction. Chlorate fires should be fought with large streams of water or with water fog. Note. See references for important precautions in the handling of potassium chlorate alone and with mixtures. The danger of spontaneous combustion with sulfur is greatly reduced by the addition of potassium bicarbonate.

12, 29, 14

Explosive Tests on Specification Grade Potassium Chlorate :

Explosion Temp. Test (5sec. value), °C: 467

Impact Test Values : (10% point)

Y.A. Apparatus, 2 kg. hammer

(22 mg. charge) ; in :

40 +

B.M. Apparatus, 2 kg. hammer, cm :

100 +

19

33

33

33

Use in Pyrotechnics : As an oxidizer and to impart a purple-red color to burning compositions.

1, 16, 17

Additional References :

- 1) "The Formation and Decomposition of Potassium Perchlorate and a New Determination of the Heat of Decomposition," C.A. 27, 1264 (1933)
- 2) "Refinement of the Crystal Structure of Sodium Chlorate and Potassium Chlorate," J. G. Bower et al., Univ. of California, AFOSR Number TN-59-104, ASTIA Document Number AD 210, 386 (1959)
- 3) "Hygroscopic Properties of Sodium, Potassium and Ammonium Nitrates, Potassium Chlorate and Mercury Fulminate," C. B. Taylor and W. C. Cope, Met. & Chem. Eng. 15, 141 (1916)
- 4) G. Ramachandran and M. Lonappan, Acta. Cryst. 10, 281 (1957)

POTASSIUM NITRATE, KNO_3
(Saltpeter, Niter)

Refs.
1, 29

Percent Oxygen:	47.48	
Specification No.:	MIL-P-156B	
The spec. covers three classes of about equal purity but of different granulation. Class 2 is used in pyrotechnics.		
Molecular Weight:	101.10	
Crystalline Form:	rhombic or trigonal	1
Color:	colorless	1
Density, g./ml. : (solid) 2.109; (liquid) $2.123 - .755 \times 10^{-4}t^\circ\text{C}$ (over the range 350–565°C)		1 40V2
Coefficient of Thermal Expansion, cubical, 0–100°C:	1967×10^{-7}	1
See also Ref. 54V2		
Heat of Formation, Kcal./mole at 298°K:	-117.76	1, 9
Free Energy of Formation, Kcal./mole at 298°K:	-93.96	1, 9
Entropy, cal./deg./mole at 298°K:	31.81	3
See table below		
Melting Point:	611°K (338°C)	7
Heat of Fusion, cal./mole:	2800	4
Boiling Point:	decomposes at 673°K (400°C)	1 4 4 4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
350	1230	3.80	600	9660	22.36
400	2490	7.17	611 (β) . . .	9970	22.87
401 (α) . . .	2520	7.24	611 (1) . . .	12,770	27.45
401 (β) . . .	3920	10.73	700	15,400	31.46
500	6780	17.11			

Potassium Nitrate, KNO₃ (page 2)

Heat Capacity, cal./deg./mole : (solid) α = 23.01 (liquid) 29.50 4, 5
 β = 28.8

See table above

Decomposition Temperature, °C : 400 1

Decomposition Products: From 650 to 750°C. The products of decomposition are KNO₂ + O + traces of NO₂. At 800°C decomposition is more extensive with KNO₂ decomposing to form K₂O, N₂, and O. 35

For DTA and TGA see Refs. 33 and 47 .

Vapor Pressure : —

X-Ray Crystallographic Data :

System	Space Group	a	Axial Angle	Molecules/ Unit Cell	1
hexagonal	C _{3v} ⁵	4.365	$\alpha = 76^\circ 56'$	1	

Hygroscopicity: Gain in mg./g. at R.T. after equilibrium has been established in vacuum desiccators. 32

% R.H.	65	75	86	99
Time	24 hrs. equil.	24 hrs. equil.	24 hrs. equil.	24 hrs. equil.
Spec. grade	— <1	— 0.2	— —	56.2 —
Purified	— —	— —	— <.1	— <.1

Critical R.H.: Specification grade, 91.7% at 20.0°C 32

Purified material, 91.8% at 26.2°C

Water absorbed by 2.0000 g. at 25°C (C.P. material) :

Fineness	Hrs.	H ₂ O absorbed, g.
40-80 mesh	2¾	0.0147
	18¾	0.1136
	25¼	0.1527
	42¾	0.2687
	47	0.2896
ground	7¼	0.0453
very	16½	0.1056
fine	40½	0.2580

Specification Grade, gain % at 70°F and 90% R.H.:

0.76 33

Solubility Data: In water (g.100/ml.): 13.3 at 0°C, 31.6 at 20°C, and 247 at 100°C 1

In alcohol and ether: insoluble

Health Hazard.: Ingestion of large amounts may cause violent irritation of the intestinal lining. Prolonged exposure to small amounts may result in anemia and nephritis. Moderately poisonous on ingestion or inhalation. 12, 29, 93

Potassium Nitrate, KNO_3 (page 3)

Safety Classifications:

OSM: Class 1. Class 2 when not packed or stored in original shipping containers.

YCC: Listed under "Explosives and Other Dangerous Articles" as oxidizing material ;yellow label.

Fire and Explosion Hazard : Dangerous, as it is a fire and explosion hazard. As an oxidizer it can give up its oxygen to other materials to produce a vigorous reaction which may result in detonation. Toxic fumes are emitted on decomposition.

12, 14

Potassium nitrate is a strong oxidizer, sensitive to shock, and can be easily detonated. When mixed with flammable materials it becomes very sensitive.

Electrostatic Sensitivity :

Use in Pyrotechnics : As an oxidizer and to impart a purple-red color to burning compositions.

17

Additional References:

- 1) "The Kinetics of Thermal Decomposition of Potassium Nitrate and of the Reaction between Potassium Nitrate and Oxygen," E. Freeman, J. Am. Chem. Soc. **79,838 (1957)**
- 2) "Simple Method for Derivative Thermal Analysis," E. Freeman and D. Edelman, Anal. Chem. **31,624 (1959)**
- 3) "Instrumentation and Applications to Thermogravimetry and Differential Thermal Analysis," C. Campbell et al., Anal. Chem. **31,1189 (1959)**
- 4) "A Thermoanalytical Study of the Ignition and Combustion Reactions of Black Powder," C. Campbell and G. Weingarten, Trans. Faraday Soc. **55, No. 444,2221 (1959)**
- 5) "Hygroscopic Properties of Sodium, Potassium and Ammonium Nitrates, Potassium Chlorate and Mercury Fulminate," G. B. Taylor and W. C. Cope, Met. & Chem. Eng. **15,141 (1916)**

POTASSIUM OXIDE, K₂O
(Potassium Monoxide)

Refs.

Specification No. :	_____	1
Molecular Weight :	94.20	
Crystalline Form :	cubic	1
Color :	colorless to grey	1, 44V22I
White at ordinary temp., yellow when hot.		
Density, g./ml. :	(solid) 2.32°	1
Coefficient of Thermal Expansion :	_____	
Heat of Formation, cal./mole at 298°K :	-86,400 (± 2000)	2
See table below		
Free Energy of Formation, cal./mole at 298°K :	-76,300 (± 2800)	2
See table below		
Free Energy Equations :		
	<i>Reaction</i>	<i>Range of Validity, °K</i>
1)	2K (c) + ½ O ₂ (g) = K ₂ O (c) Δ F _T ^o = - 86,400 + 33.901'	298.16-336.4
2)	2K (l) + ½ O ₂ (g) = K ₂ O (c) Δ F _T ^o = - 87,380 + 1.15T log T + 33.901'	336.4-1049
3)	2K (g) + ½ O ₂ (g) = K ₂ O (c) Δ F _T ^o = - 103,090 - 16.12T log T + 129.641'	1049-1500

HEAT AND FREE ENERGY OF FORMATION OF K₂O (c)

T, °K	Δ H (cal./mole)	Δ F ^o (cal./mole)
298.16	-86,400 (± 2000)	-76,300 (± 2800)
336.4	-86,400	-75,000
336.4	-87,600	-76,000
400	-87,600	-72,600
500	-87,600	-68,900
600	-87,700	-65,100
700	-87,700	-61,400
800	-87,800	-57,600
900	-87,800	-53,800
1000	-87,900	-50,000
1049	-87,900	-48,200
1049	-125,800	-48,200
1100	-125,400	34,400
1200	-124,700	-37,100
1300	-124,000	-29,800
1400	-123,300	-22,600
1500	-122,600	-15,400

Phase changes of Metal

M.P. 336.4°K ; Δ H = 558 cal./g.-atom
B.P., 1049°K ; Δ H = 18,925 cal./g.-atom

Potassium Oxide, K₂O (page 2)

Entropy, cal./deg./mole at 298°K :	23.5 ± 2.5	24
Melting Point :	—	
Heat of Fusion :	not obtainable	7
Boiling Point :	—	
Transition Point :	1253°K (980°C)	6
Heat of Transition, Kcal./mole :	6.8	6
Heat of Sublimation :	—	
Heat Content or Enthalpy :	—	
Heat Capacity :	—	
Decomposition Temperature :	below 763°K at 1750 ± 100°K	8 7
Decomposition Products :	—	
Vapor Pressure of alkali oxide and alkali metal in equil. with solid alkali oxide, atm. at 1000°K (calcd.) :		Adnl. Ref. 5
X-Ray Crystallographic Data :		
System cubic	Space Group a 6.436	Molecules/Cubic Cell 18
Hygroscopicity :	Reacts with water to form KOH with evolution of considerable heat,	
Solubility Data :	Very soluble in water and is slightly soluble in alcohol and ether.	
The heat of solution in water, Kcal./mole :	75	44V22 I 12, 25, 29
Health Hazard :	Has a caustic reaction on the skin and respiratory system. Because it causes dermatitis, avoid its dust and treat exposed skin with large quantities of water.	
Safety Classifications :		
OSM :	not listed	
ICC :	not listed	
Caustic potash liquid is classified under "Explosives and Other Dangerous Articles" as a corrosive liquid.		
Fire and Explosion Hazard :	Considerable heat is developed by reaction with water. Highly caustic.	12
Electrostatic Sensitivity :	—	
Use in Pyrotechnics :	a product of burning potassium compounds	
Additional References :		
1) "Stability of Solid and Gaseous Alkali and Alkaline Earth Oxides," L. Brewer and D. F. Mastick, J. Am. Chem. Soc. 73, 2045 (1951)		

POTASSIUM PERCHLORATE, KClO_4
(Potassium Hyperchlorate)

Refs.

Percent Oxygen :	46.19	
Specification No. :	JAN-P-217 (2)	
The spec. covers one grade and four granulations.		
Molecular Weight :	138.55	
Crystalline Form :	rhombic	1
Color :	colorless	1
Density, g./ml. :	(solid) 2.52	1
Coefficient of Thermal Expansion, cubical, from -78° to $+18^\circ\text{C}$:	14×10^{-5}	44V22 I
Heat of Formation, Kcal./mole at 298°K :	-103.6	1, 9
Free Energy of Formation, Kcal./mole at 298°K :	-72.7	1, 9
Entropy, cal./deg./mole at 298°K :	36.1	1, 8, 9
Melting Point :	337°K ($610 \pm 10^\circ\text{C}$)	1
Literature values vary from $< 400^\circ$ to 610°C , with and without mention of decomposition.		65
Heat of Fusion:	—	
Boiling Point:	decomposes at 926°K (653°C)	Addnl. Ref. 7
Transition Point:	α (rhombic) to β (cubic) at 572°K (299°C)	9
Heat of Transition, Kcal./mole :	3.29	9
Heat of Sublimation :	—	
Heat Content or Enthalpy :	—	
Heat Capacity, cal./deg./mole :	(solid) 26.33	4, 9 Addnl. Ref. 4
Decomposition Temperature, $^\circ\text{C}$:	Starts at about 530° and is complex.	47
See Addnl. Ref. 10 for TGA		
Heat of Decomposition of Perchlorates, Kg. cal./mole (constant volume) at room temperature, $\text{KClO}_4 \rightarrow \text{KClO}_2 + \text{O}_2$:	1.73	Addnl. Ref. 8
Decomposition Products :	$\text{KCl} + 4\text{O}$	20
Vapor Pressure:		
See 54V1		
X-Ray Crystallographic Data :		
<i>System</i>	<i>Space Group</i>	<i>Molecules/ Unit Cell</i>
rhombic	V_h^{16}	4
cubic (340°C)	T_d^{16} or T^2	
	D_{2h}^{16}	4
	8.834 5.650 7.240	
	7.47	
	8.857 5.663 7.254	
		Addnl. Ref. 9 97V6

Potassium Perchlorate, KClO₄ (page 2)

Hygroscopicity : Gain (mg./g.) at 23–5°C and 98% R.H. after equilibrium has been established in a vacuum desiccator.		32
Spec. grade, after 24 hrs. :	1	
Purified, at equilibrium :	< 1.0	
Critical R.H. of spec. grade material :	99.3% at 26.2°C	32
Solubility Data : In water, g./100 ml. :	0.75 at 0°C and 21.8 at 100°C	1, 65
Solubility in Nonaqueous Solvents at 25°C :		
<i>Solvent</i>	<i>g./100 g. of solvent</i>	65
Acetone	0.155	72
Eethyl acetate	0.0015	77
Ethyl alcohol	0.012	
Ethyl ether	insoluble	
Methyl alcohol	0.105	
Ethyl glycol	1.03	
Health Hazard : Moderately toxic and irritating to the skin, mucous membranes, and respiratory tract. It may affect the kidneys. Avoid contact with KClO ₄ . The probable lethal dose for humans is 50–500 mg./kg.		93, 12, 29, 65
Safety Classifications:		
OSM: Class 1. Class 2 when not packed in original shipping containers or equivalent.		
ICC: Listed under Explosives and Other Dangerous Materials. Classed as oxidizing material ;yellow label.		
Fire and Explosion Hazard: A fire and explosive hazard, particularly when mixed with organic material, finely divided metals or sulfur. When heated it emits highly toxic fumes. For fighting a fire or potassium perchlorate alone use water.		12, 14
Electrostatic Sensitivity :	—	
Impact Tests: Charge weight = 0.023 g.		33
Bureau of Mines Apparatus, 2 kg. wt., cm.:	(10% point) 100 +	
P.A. Apparatus, 2 kg. wt., in.:	(10% point) 40 +	
Use in Pyrotechnics: As an oxidizer and to color burning compositions purple-red.		
Additional References:		
1) Ref. 47		
2) "Simple Method for Derivative Differential Analysis," E. Freeman and D. Edelman, Anal. Chem. 31, 624 (1959)		
3) M. M. Markowitz, J. Phys. Chem. 61, 505 (1957)		
4) L. L. Bircumshaw and B. H. Newman, Proc. Royal Society (London) A227, 115 (1954)		
5) A. E. Harvey et al., J. Am. Chem. Soc. 76, 3270 (1954)		

Potassium Perchlorate, KClO_4 (page 3)

- 6) "Precise Studies of the Crystal Structures of Lithium Perchlorate Trihydrate, Anhydrous Lithium Perchlorate, and Potassium Perchlorate," R. J. Prosen and K. N. Trueblood, Perchlorates TN-2, OSRTN 56-563, ASTIA Document No. AD 110-384 (1956)
- 7) C. Duval, C.A. 42, 8698 (1948)
- 8) K. A. Hoffman and P. H. Marin, C.A. 27, 1264 (1933)
- 9) "The *Crystal* Structure of Potassium Perchlorate— KClO_4 ," N. V. Mani, Proceedings of the Indian Academy of Science, pp. 143-151 (1967)
- 10) Anal. Chem. Acta 2, 105 (1948)

SHELLAC

(For trade names and manufacturers, see Ref. 60)

Refs

Shellac is a variable natural product obtained from various species of *Acacia*.

Shellac is the only resinous substance of animal origin. It is produced by an insect (*Tachadia lacca*) which lives on certain trees of southern Asia. The insect takes up sap through its stinger and after a semi-polymerization process exudes it as a gum. This lac secretion coats their bodies and the twigs of the trees with a heavy incrustation which is scraped off and forms the commercial slick lac. This contains not only the lac resin but also woody matter, lac dye, and the bodies of insects. The seed lac is ground and washed to remove the wood and most of the coloring matter. Shellac is prepared from the seed lac by melting or by extraction with solvents. The molten material is spread over a hot cylinder, stretched, and cooled. The cooled sheet is then broken into flakes of shellac. After purification, shellac varies in color from orange to lemon yellow. Orange shellac may contain as much as 1% of powdered orpiment (As_2O_3).

16, 20, 59,
52V7

Chemically, shellac contains condensed long chain esters of condensed polyhydroxy acids together with rosin and wax. By solvent action the wax content of the seed lac is reduced to 1%. Shellac is graded by color and amount of dirt. The best grade contains no resin, but in inferior grades the resin content may be as high as 12%.

Characteristics of Shellac (analytical):

Acid Number:	48-64
Ester Number:	137-63
Saponification Number:	194-213
Iodine Number:	185-210

1
1
1
29

Specification No.: MIL-S-20526

(Includes U.S. Army Specification No. 50-11-17A)

The spec. covers three grades which differ in purity. Grade A is used in both primer pyrotechnic compositions. Grade A includes the grades of orange shellac known as "Double Triangle G," "Diamond I," "Superfine," the highest grades, "D.C." and "V.S.O." The so-called machine-made shellacs, such as "CV" and "CVTN," in general fall under Grade A.

Molecular Weight:	—
Crystalline Form:	—
Color:	pale orange to lemon yellow
Density, g./ml.:	(solid) 1.08-1.13
Coefficient of Thermal Expansion:	—
Heat of Formation:	—
Free Energy:	—
Entropy:	—
Melting Point:	indefinite 388-393°K (115-120°C)
Heat of Fusion:	—
Boiling Point:	decomposes

59
1

20, 9

Shellac (page 2)

Transition Point :	_____	
Heat of Sublimation :	_____	
Heat Content or Enthalpy :	_____	
Heat Capacity :	_____	
Decomposition Temperature :	_____	
Decomposition Products :	_____	
Vapor Pressure :	_____	
X-Ray Crystallographic Data :	_____	
Hygroscopicity : Nonhygroscopic and not altered on exposure to the air,		1
Solubility Data, g./100 g. solution :		29
In water:	insoluble	
In alcohol:	85-90 (<i>very slowly soluble</i>)	
In ether:	13-15	
In benzene:	10-20	
Sparingly soluble in oil or turpentine. Soluble in aqueous ethanolamines, alkalis, or borax. Solubility in petroleum ether, 2-6 g./100 g. solution. Soluble in the lower aliphatic alcohols but not in hydrocarbons.		29, 53
Health Hazard :	none	
Safety Classifications:		
OSM :	not listed	
ICC :	not listed	
Fire and Explosion Hazard : Easily ignited and continues to burn.		60
Ignition Temp. of Dust Cloud, °C :	390	26
Minimum Explosive Concentration of Dust, mg./l. :	15	26
Electrostatic Sensitivity, minimum energy required for ignition of dust cloud by electric sparks (millijoules) :	10	26
Use in Pyrotechnics: As a binder, a fuel retardant, and to reduce absorption of moisture. It is applied as an alcoholic solution. The alcohol is allowed to evaporate after application.		20V1, 20V3

SILICON. Si

Specification No.:	JAN-S-230 and Amendment 1	
Amendment 1 lists two grades differing slightly in purity, and four classes differing in granulation.		
Molecular Weight:	28.09	
Crystalline Form:	Needle-like crystals or octahedral platelets (cubic). Occurs in three forms; adamantine (cubic), amorphous, and graphitoidal.	1, 29
Color:	Lustrous black to gray. The amorphous form is a dark brown powder, steel grey, black plates.	1, 29
Types and Differences of Behavior:	Brown amorphous silicon dissolves in molten metals and burns in air to form SiO ₂ . Black, shiny graphitoidal silicon is not easily oxidized and not attacked by the common acids, but is soluble in alkalis. Crystalline silicon is obtained in dark, steel-grey globules or six-sided pyramids. It is less reactive than the amorphous form, but is attacked by boiling water. The three forms are obtained by reduction. Commercial silicon is the graphitoidal flake form and when refined contains 97% Si and less than 1% iron.	16, 29
Density, g./ml.:	(solid) adamantine, 2.42 amorphous, 2.08 graphitoidal, about 2.4	1
Coefficient of Thermal Expansion, linear at 25°C:	4.2×10^{-6}	29
40°C:	7.63×10^{-6}	1
Heat of Formation, Kcal./mole at 298°K:	(gas) 880.4	1, 9
Free Energy of Formation, Kcal./mole at 298°K:	(gas) 77.41	1, 9
Entropy, cal./deg./mole at 298°K:	(gas) 40.12 (c) 4.53	1, 5, 9 1, 5, 9
See Table a		
Melting Point:	1685°K (1412°C)	4
Heat of Fusion, cal./mole:	12,100	4
Boiling Point:	2950°K (2677°C)	5
Heat of Vaporization, Kcal./mole:	about 72.6	40V2
Transition Point:	none up to 1273°K (1000°C) about 2873°K (2600°C)	Addnl. Ref. 1 40
Heat of Sublimation, Kcal./mole:	(monatomic Si) 105	5
Heat Content or Enthalpy, cal./mole at 298°K:	(solid) 769	

a. HEAT CONTENT AND ENTROPY OF Si (c, 1)
(Base, crystals at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	515	1.48	1400	6680	9.04
500	1060	2.69	1500	7340	9.49
600	1630	3.73	1600	8010	9.92
700	2220	4.64	1685 (c)	8580	10.27
800	2830	5.46	1685 (l)	20,680	17.45
900	3450	6.19	1700	20,770	17.50
1000	4080	6.85	1800	21,380	17.85
1100	4720	7.46	1900	21,990	18.18
1200	5360	8.02	2000	22,600	18.49
1300	6020	8.65			

b. HEAT CONTENT AND ENTROPY OF Si (g)
(Base, ideal gas at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	535	1.54	1900	8140	9.48
500	1045	2.68	2000	8665	9.70
600	1555	3.61	2200	9715	10.20
700	2060	4.39	2400	10,780	10.67
800	2580	5.06	2600	11,850	11.10
900	3060	5.65	2800	12,935	11.50
1000	3565	6.18	3000	14,020	11.87
1100	4065	6.66	3500	16,765	12.71
1200	4565	7.09	4000	19,520	13.45
1300	5070	7.49	4500	22,280	14.10
1400	5575	7.85	5000	25,040	14.69
1500	6085	8.22	6000	30,555	15.69
1600	6595	8.55	7000	36,105	16.55
1700	7105	8.86	8000	41,845	17.31
1800	7625	9.15			

Silicon, Si (page 3)

Si (g):									
Enthalpy : $H_T - H_{298.15} = 4.82T + 0.09 \times 10^{-3}T^2 - 0.42 \times 10^5T^{-1} - 1304$ (0.3percent ; 298-5000°K)									
Heat Capacity: $C_p = 4.82 + 0.18 \times 10^{-3}T + 0.42 \times 10^5T^{-2}$									
Heat Capacity, cal./deg./mole at 298°K :									
					(solid)	4.80	5		
					(liquid)	7.0			
					(gas)	5.32			
Also see above									
Decomposition Temperature :								—	
Decomposition Products :								—	
Vapor Pressure :									
Press. mm.	1	10	40	100	400	760	M.P.	1	
Temp. °C	1724	1888	2000	2083	2220	2287	1420		
at melting point, mm.								0.075	33
X-Ray Crystallographic Data :									
System	Space Group		a		Atoms/ Unit Cell				
cubic	O _h		5.4173		8			1	
Hygroscopicity (milled Si), cumulative increase in weight after :									
storage over H ₂ O for 18days				3 days in oven at 105°C					
4.3%				0.4%				50	
(Some caking of powder noted.)									
Solubility data :									
in water:				insoluble				1	
in molten alkali oxide, HF:				soluble				29	
Health Hazard :				slight				12,295	
Safety Classifications :									
OSM :				Class 2					
ICC :				not listed. Probably classed					
				as a flammable solid					
U.N.:				inflammable solid					
Fire and Explosion Hazard: Powdered silicon when heated in the air is a dangerous fire hazard. It burns with intense heat and reacts explosively with oxidizing materials, and with water or steam. Prevent water from contacting the material. Store and process only in a room or building adequately vented at the highest point to prevent accumulation of hydrogen gas which results from the reaction of powdered metal and moisture. In the repair or maintenance of buildings or equipment, powder or dust should be removed and nonsparking tools used.								12, 14	
The powder is moderately explosive.								49, 51	
Electrostatic Sensitivity, minimum energy required for ignition of powder by electric sparks, millijoules for dust cloud :								80	26
Ignition Temperature, °C :								(dust cloud) 775 (dust layer) 950	26
Minimum Explosive Concentration of powdered silicon, mg./l :								100	26
Use in Pyrotechnics :								as a fuel	
Additional References :									
1) J. Phys. Chem. 60, 509 (1956)									

SILICON DIOXIDE, SiO ₂				<i>Kefs.</i>
(Quartz, Silica, Silicic Anhydride, Rock Crystal, Cristobalite)				1, 12
Percent Oxygen :	53.25			
Specification No. :	—			
Molecular Weight :	60.06			
Crystalline Form :				1
Type of SiO ₂	Crystalline Form	Density	M.P. °C	
cristobalite	cubic or tetragonal	2.32	1710	
lechatelierite		2.20		
quartz	hexagonal	2.653-2.660	< 1470	
tridymite	rhombic	2.28-2.33	1670	
Color :	colorless			1
Density, g./ml. :	(solid) 2.653-2.660			1
See table above				
Coefficient of Thermal Expansion :				1
quartz (c), -190° to +16°C :	5.21 × 10 ⁻⁶			
parallel to axis, 0-80°C :	7.97 × 10 ⁻⁶			
perpendicular to axis, 0-80°C :	13.31 × 10 ⁻⁶			
fused, -191° to +16°C :	0.256 × 10 ⁻⁶			
0-30°C :	0.42 × 10 ⁻⁶			
0-100°C :	0.50 × 10 ⁻⁶			
0-800°C :	0.546 × 10 ⁻⁶			
0-1200°C :	0.585 × 10 ⁻⁶			
cubic expansion, quartz, 50-60°C :	0.3538 × 10 ⁻⁶			
Heat of Formation, Kcal./mole at 298°K :	quartz, -205.4			1, 9
	cristobalite, -205.0			1
Free Energy of Formation, Kcal./mole at 298°K :	quartz, -192.4			1
	cristobalite, -192.1			
	tridymite, -191.9			
a. HEAT AND FREE ENERGY OF FORMATION OF SiO ₂ (α-quartz, β-quartz, l)				2
T, °K	A H (cal./mole)	Δ F° (cal./mole)		
298.16	-239,900 (± 1000)	-196,900 (± 1000)		
400	-209,900	-192,500		
500	-209,800	-188,100		
600	-209,700	-183,800		
700	-209,500	-179,500		
800	-209,200	-175,200		
848	-209,000	-173,200		
848	-208,700	-173,200		
900	-208,600	-171,000		
1000	-208,400	-166,800		
1100	-208,300	-162,700		
1200	-208,100	-158,500		
1300	-209,900	-154,400		

Silicon Dioxide, SiO₂ (page 2)

T, °K	Δ H (cal./mole)	A F° (cal./mole)
1400	-207,800	-150,300
1500	-207,600	-146,200
1600	-207,400	-142,100
1683	-207,300	-138,700
1683	-218,400	-138,700
1700	-218,300	-138,000
1800	-218,200	-133,208
1883	-218,100	-129,300
1883	-216,000	-129,300
1900	-215,900	-128,500
2000	-215,200	-123,900

Phase changes of Oxide

T.P. (α-quartz to p-quartz), 848°K; Δ H = 290 cal./mole

T.P. (p-quartz to p-tridymite), 1140°K; Δ H = 180 cal./mole

M.P., 1883°K; Δ H = 2040 cal./mole

b. HEAT AND FREE ENERGY OF FORMATION OF SiO₂
(α-cristobalite; p-cristobalite)

T, °K	Δ H (cal./mole)	A F° (cal./mole)
298.16	-209,550 (± 250)	-196,650 (± 300)
400	-209,600	-192,200
500	-209,500	-187,900
523	-209,450	-186,900
523	-209,250	-186,900
600	-209,100	-183,600
700	-208,900	-179,350
800	-208,700	-175,150
900	-208,500	-171,000
1000	-208,300	-166,800
1100	-208,100	-162,700
1200	-207,950	-158,550
1300	-207,750	-154,450
1400	-207,550	-150,356
1500	-207,350	-146,300
1600	-207,200	-142,200
1683	-207,050	-138,850
1683	-218,150	-138,850
1700	-218,100	-138,050
1800	-218,000	-133,350
1900	-217,850	-128,650
2000	-217,700	-123,950

Phase changes of Oxide

T.P., 523°K; Δ H = 200 cal./mole

c. HEAT AND FREE ENERGY OF FORMATION OF SiO₂
(α -trid., β -trid., l)

T, °K	ΔH (cal./mole)	ΔF° (cal./mole)
298.16	-209,400 (± 1000)	-196,500 (± 1000)
390	-209,400	-192,600
390	-209,400	-192,600
400	-209,400	-192,100
500	-209,200	-187,800
600	-209,100	-183,600
700	-208,900	-179,400
800	-208,700	-175,200
900	-208,500	-171,000
1000	-208,300	-166,800
1100	-208,100	-162,700
1200	-207,900	-158,600
1300	-207,700	-154,400
1400	-207,500	-150,400
1500	-207,300	-146,300
1600	-207,200	-142,200
1683	-207,000	-138,800
1683	-218,100	-138,800
1700	-218,000	-138,000
1800	-218,000	-133,400
1900	-217,800	-128,700
1953	-217,700	-126,200
1953	-215,600	-126,200
2000	-215,200	-123,900

Phase changes of Oxide

T.P. (α -trid. to β -trid.), 390°K ; $\Delta H = 40$ cal./moleT.P. (β -trid. to β -crst.), 1743°K ; $\Delta H = 30$ cal./moleM.P., 1953°K ; $\Delta H = 2150$ cal./mole

Free Energy Equations :

Reaction	Range of Validity, °K
1) Si (c) + O ₂ (g) = SiO ₂ (a-quartz)	298.16-848
$\Delta F_T^\circ = -210,070 + 3.981 \log T - 3.32 (10^{-3}T^2) + 6.05 (10^5T^{-1}) + 34.59T$	
2) Si (c) + O ₂ (g) = SiO ₂ (β -quartz)	848-1683
$\Delta F_T^\circ = -209,920 - 3.36T \log T - .19 (10^{-3}T^2) - .745 (10^5T^{-1}) + 53.44T$	
3) Si (l) + O ₂ (g) = SiO ₂ (p-quartz)	1683-1883
$\Delta F_T^\circ = -219,000 + .58T \log T - .47 (10^{-3}T^2) - .20 (10^5T^{-1}) + 46.58T$	
4) Si (l) + O ₂ (g) = SiO ₂ (l)	1883-2000
$\Delta F_T^\circ = -228,590 - 15.66T \log T + 103.97T$	
5) Si (c) + O ₂ (g) = SiO ₂ (a-cristobalite)	298.16-523
$\Delta F_T^\circ = -207,330 + 19.96T \log T - 9.75 (10^{-3}T^2) - .745 (10^5T^{-1}) - 9.78T$	

Silicon Dioxide, SiO₂ (page 4)

- 6) Si (c) + O₂ (g) = SiO₂ (p-cristobalite) 523-1683
 $\Delta F_T^\circ = -209,820 - 3.341 \log T - .24 (10^{-3}T^2) - .745 (10^5T^{-1}) + 53.35T$
- 7) Si (4) + O₂ (g) = SiO₂ (p-cristobalite) 1683-2000
 $\Delta F_T^\circ = -218,900 + .60T \log T - .52 (10^{-3}T^2) - .20 (10^5T^{-1}) + 46.49T$
- 8) Si (c) + O₂ (g) = SiO₂ (α-tridymite) 298.16-390
 $\Delta F_T^\circ = -207,030 + 22.291 \log T - 11.62 (10^{-3}T^2) - .745 (10^5T^{-1}) - 15.641T$
- 9) Si (c) + O₂ (g) = SiO₂ (p-tridymite) 390-1683
 $\Delta F_T^\circ = -209,350 - 1.59T \log T - .54 (10^{-3}T^2) - .745 (10^5T^{-1}) + 47.861T$
- 10) Si (1) + O₂ (g) = SiO₂ (p-tridymite) 1683-1953
 $\Delta F_T^\circ = -218,430 + 2.351 \log T - .82 (10^{-3}T^2) - .20 (10^5T^{-1}) + 41.00T$

Entropy, cal./deg./mole at 298°K :

quartz, 10.00
cristobalite, 10.19
tridymite, 10.36

1, 9
1
1

See Table d

Melting Point:

See Crystalline Form

Heat of Fusion, Kcal./mole at 298°K :

quartz, 2.04
cristobalite, 3.6 ± 0.5
2503°K (2230°C)

9
24
1

Boiling Point :

Heat of Vaporization :

Heat of Sublimation:

—

4

	cal./mole	cal./deg. mole		cal./mole	S _T - S _{298.15} cal./deg. mole
400	1210	3.48	1200	14,080	20.90
500	2560	6.48	1300	15,790	22.27
523 (α) . . .	2910	7.16	1400	17,510	23.54
523 (β) . . .	3110	7.54	1500	19,240	24.74
600	4310	9.68	1600	20,990	25.87
700	5850	12.05	1700	22,750	26.93
800	7460	14.20	1800	24,530	27.95
900	9090	16.12	1900	26,320	28.92
1000	10,730	17.85	2000	28,120	29.84
1100	12,390	19.43			

SiO₂ (α-cristobalite)

Enthalpy : H_T - H_{298.15} = 4.281' + 10.53 × 10⁻³T² - 2212 (10 percent ; 298-523°K)

Heat Capacity: C_p = 4.28 + 21.06 × 10⁻³T ; A H₅₂₃ (transition) = 200

Silicon Dioxide, SiO₂ (page 5)

4

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	1230	3.54	1300	15,450	21.57
500	2550	6.48	1400	17,240	22.90
600	3950	9.03	1500	19,080	24.17
700	5430	11.31	1600	20,980	25.39
800	6990	13.39	1700	22,930	26.57
900	8610	15.30	1800	24,920	27.71
1000	10,280	17.06	1900	26,950	28.81
1100	11,980	18.68	2000	29,010	29.87
1200	13,700	20.17			

SiO₂ (gl) :

Enthalpy : $H_T - H_{298.15} = 13.38T + 1.84 \times 10^{-3}T^2 + 3.45 \times 10^5T^{-1} - 5310$
(0.4 percent ; 298-2000°K)

Heat Capacity : $C_p = 13.38 + 3.68 \times 10^{-3}T^2 - 3.45 \times 10^5T^{-2}$

f. HEAT CONTENT AND ENTROPY OF SiO₂ (tridymite)
(Base, α-crystals at 298.15°K)

4

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
350	585	1.81	1100	12,250	19.25
390 (α) . . .	1085	3.16	1200	13,940	20.72
390 (β) . . .	1125	3.26	1300	15,650	22.09
400	1270	3.63	1400	17,370	23.37
500	2710	6.84	1500	19,100	24.56
600	4170	9.50	1600	20,860	25.69
700	5710	11.87	1700	22,610	26.75
800	7320	14.02	1800	24,390	27.77
900	8954	15.94	1900	26,180	28.74
1000	10,590	17.67	2000	27,980	29.66

SiO₂ (a-tridymite)

4

Enthalpy : $H_T - H_{298.15} = 3.27T + 12.40 \times 10^{-3}T^2 - 2077$ (0.2 percent ; 298-390°K)

Heat Capacity : $C_p = 3.27 + 24.80 \times 10^{-3}T$; A H_{390} (transition) = 40

SiO₂ (p-tridymite) :

Enthalpy : $H_T - H_{298.15} = 13.64T + 1.32 \times 10^{-3}T^2 - 4395$ (0.7 percent ; 390-2000°K)

Heat Capacity : $C_p = 13.64 + 2.64 \times 10^{-3}T$

Silicon Dioxide, SiO₂ (page 6)

Transition Point, °K: c, III 91 → c, II 846 → c, I 1140 tridymite, c, I

Heat of Transition, Kcal./mole: 0.15 0.12

Heat Capacity, cal./deg./mole: (solid) 10.62
(gas) 7.14

See Tables d, e, f

Decomposition Temperature: At 1173–1428°K and at 1900°K the gas is SiO.

Decomposition Products: —

Dissociation Pressures: —

Vapor Pressure: —

Press. mm.	10	40	100	400	760	M.P.
Temp. °C	1732	1867	1969	2141	2227	1710

X-Ray Crystallographic Data:

Substance	System	Space Group	a	b	c	Molecules/Unit Cell
p-cristobalite (at 290°C)	cub	O _h ¹	7.12			8
α-quartz	hex	D _{3d} ⁴ or D _{3d} ⁶	4.903		5.393	3
β-quartz (at 600°C)	hex	D _{6h} ⁴ or D _{6h} ⁶	5.01		5.47	3
α-tridymite	rhomb	D _{2h} ⁴	9.88	17.1	16.3	64
β-tridymite	hex	D _{6h} ⁴	5.03		8.22	64

Hygroscopicity: —

Solubility Data: Soluble in HF; very slightly soluble in alkalis. Insoluble in water and acids. For the effect of particle size on the soly. of amorphous SiO₂ in water see Addnl. Ref. 1.

Health Hazard: Prolonged exposure to SiO₂ dust causes disabling pulmonary fibrosis (silicosis). The presence of other dusts may reduce the action of the silica: this is particularly so with small amounts of Al dust.

M.A.C., million particles per cu. ft. of air for an 8 hr. working day.

Silica—high (above 50% free SiO₂): 5

medium (5 to 50% free SiO₂): 20

Low (below 5% free SiO₂): 50

Safety Classifications: none listed in O.S.N., I.C.C. or U.N.

Fire and Explosion Hazard: —

Electrostatic Sensitivity: —

TEMPERATURE STABILITY OF ALLOTROPIC FORMS OF SiO₂

Form	Temperature Stability
Low (α) quartz	Stable at atmospheric temp. and up to 573°C.
High (β) quartz	Stable from 573 to 870°C; capable of existence above 870°C but is not stable.
Low (α) tridymite	Capable of existence at atmospheric temp. and up to 117°C, but is not stable in this range.

Silicon Dioxide, SiO_2 (page 7)

Lower-high (β_1) tridymite	Capable of existence between 117 and 163°C but is not stable in this range.
Upper-high (β_2) tridymite	Capable of existence above 163°C , and is stable from 870 to 1470°C ; above 1470°C is again unstable; melts at 1670°C.
Low (α) cristobalite	Capable of existence above 163°C , and up to 200 to 275°C but is not stable in this range.
High (β) cristobalite	Capable of existence above 200 to 275°C , and is stable from 1470 to 1710°C (M.P.) .
Vitreous silica	Capable of existence at atmospheric temps. and up to 1000°C and above where it begins to crystallize with measurable rapidity, but is an unstable undercooled liquid at all temps. below 1719°C.

Use in Pyrotechnics : A product resulting from burning silicon or silicon compounds.

Additional References :

- 1) G. B. Alexander, J. Phys. Chem. **61**, 1563-64 (1957)
- 2) Ref. 44V15B
- 3) L. Brewer and D. F. Mastick, J. Chem. Phys. **19**, **834** (1951)
- 4) "Crystal Chemistry in Ceramics: VI Polymorphism," W. Hauth Jr., Bull. Am. Ceram. Soc. **50**, (5) 165-67 (1951) . Cited by Ref. 65.
- 5) 97V1

SODIUM, Na		(Sodium)	
Specification No.:	JAN-S-328		
Molecular Weight:	22.991		
Crystalline Form:	cubic		
Color:	Silvery metal when freshly cut; tarnishes rapidly on exposure to air.		
	becoming dull and grey.		
Density, g./ml.:	(solid) 0.9735		
Coefficient of Thermal Expansion, linear, -188° to +17°C:	6.2×10^{-6}		
Heat of Formation, Kcal./mole at 298°K:	(monatomic gas) 25.9		
	(diatomic gas) 33.8		
Free Energy of Formation, Kcal./mole at 298°K:	(monatomic gas) 18.595		
	(diatomic gas) 24.685		
Entropy, cal./deg./mole, at 298°K:	(monatomic gas) 36.71		
	(diatomic gas) 33.8		
	(c) 12.21		
See Tables a, b, and c			
Melting Point:	370.97°K (97.81°C)		
Heat of Fusion, cal./mole:	622		
Boiling Point:	1178°K (905°C)		
Heat of Vaporization, cal./mole:	23,380		
Transition Point:			
Heat of Sublimation, cal./mole:	(monatomic gas) 25,900		
	(diatomic gas) 33,800		
Heat Content or Enthalpy, cal./mole at 298°K:	(solid) 1532		
See Tables a, b, c, and d			
a. HEAT CONTENT AND ENTROPY OF Na (c, l, g)			
(Base, crystals at 298.15°K)			
T, °K	H ^T - H ^{298.15}	S ^T - S ^{298.15}	
	cal./mole	cal./deg.	mole
350	360	1.11	1178 (l)
371 (c)	514	1.54	1178 (g)
371 (l)	1136	3.21	1200
400	1355	3.78	1300
500	2095	5.44	1400
600	2820	6.76	1500
700	3520	7.84	1600
800	4220	8.77	1700
900	4910	9.58	1800
1000	5595	10.31	1900
1100	6295	10.98	2000
			34,305
			33,805
			33,310
			32,815
			32,315
			31,820
			31,325
			30,825
			30,330
			30,220
			6840
			11.47
			31.32
			31.41
			31.80
			32.18
			32.52
			32.84
			33.14
			33.42
			33.69
			33.94

Sodium, Na (page 2)

Na (c) :

Enthalpy : $H_T - H_{298.15} = 4.02T + 4.52 \times 10^{-8}T^2 - 1699$ (0.3 percent ; 298–371°K)Heat Capacity : $C_p = 4.02 + 9.04 \times 10^{-8}T$

Na (l) :

Enthalpy : $H_T - H_{298.15} = 6.83T - 1.08 \times 10^5 T^{-1} - 1107$ (0.2 percent ; 371–1178°K)Heat Capacity : $C_p = 6.83 + 1.08 \times 10^5 T^{-2}$

Na (g) :

Enthalpy : $H_T - H_{298.15} = 4.97T + 24,365$ (0.1 percent ; 1178–2000°K)

b. HEAT CONTENT AND ENTROPY OF Na (g)

(Base, ideal gas at 298.15°K).

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	505	1.46	1900	7960	9.20
500	1005	2.57	2000	8460	9.46
600	1500	3.48	2200	9455	9.93
700	1995	4.24	2400	10,450	10.37
800	2495	4.90	2600	11,450	10.77
900	2990	5.49	2800	12,455	11.14
1000	3490	6.01	3000	13,470	11.49
1100	3985	6.49	3500	16,055	12.29
1200	4480	6.92	4000	18,770	13.01
1300	4980	7.32	4500	21,700	13.70
1400	5475	7.69	5000	25,015	14.40
1500	5970	8.03	6000	33,755	15.98
1600	6470	8.35	7000	46,850	18.02
1700	6965	8.65	8000	65,295	20.45
1800	7460	8.93			

Na (g) :

Enthalpy : $H_T - H_{298.15} = 4.97T - 1482$ (0.1 percent ; 298–3000°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	920	2.64	1300	9240	13.51
500	1825	4.67	1400	10,185	14.21
600	2735	6.33	1500	11,135	14.87
700	3655	7.75	1600	12,090	15.48
800	4580	8.99	1800	14,010	16.61
900	5500	10.07	2000	15,945	17.63
1000	6435	11.06	2200	17,895	18.56
1100	7360	11.94	2400	19,860	19.41
1200	8305	12.76	2600	21,845	20.21

Sodium, Na (page 3)

Enthalpy : $H_T - H_{298.15} = 8.961' + 0.18 \times 10^{-3}T^2 + 0.10 \times 10^5 T^{-1} - 2721$
(0.1 percent ; 298-2600°K)

Heat Capacity : $C_p = 8.96 + 0.36 \times 10^{-3}T - 0.10 \times 10^5 T^{-2}$

Heat Capacity, cal./mole at 298°K : (solid) 6.74 (liquid) 7.50
(gas) (monatomic) 4.97
(diatomic) 8.96

d. HEAT CAPACITY OF SODIUM

Solid, 298-371°K

Liquid, 371-1163°K

Gas (monatomic), 1163-3000°K

T, °K	C _p (cal./deg./mole)
298	6.74
300	6.75
400	7.52
600	7.10
800	6.90
1000	6.93
1100	7.01
1200-2000	4.97
2400	4.99
2800	5.04
3000	5.08

See equations above

Decomposition Temperature : —

Decomposition Products : —

Vapor Pressure:

Press.,	1	10	40	100	400	760	M.P. °C
Temp. °C	439	549	633	701	823	892	97.5

$\log P = \frac{-7812}{T} + 4.521$, where P = atm. and T = °K

X-Ray Crystallographic Data :

System Space Group a Atoms/Unit Cell

cubic O_F 4.282 2

Hygroscopicity : Reacts vigorously with water to form NaOH + H₂

Caution : keep under kerosene.

Solubility Data : In water, alcohol:

decomposes

In benzene, ether:

insoluble

Health Hazard : Extremely caustic to all tissues. Reacts exothermally with the moisture of the body or tissue surfaces causing thermal and chemical burns.

Safety Classifications :

OSM :

class 2

ICC : Listed under "Explosives and Other Dangerous Articles" as a flammable solid ;yellow label.

Sodium, Na (page 4)

Fire and Explosion Hazard : Metallic sodium has an autoignition temperature of 115° in dry air. It is dangerous when exposed to heat, flame, moisture, air, or oxidizing material. It reacts exothermally with the halogens, acids, and halogenated hydrocarbons.

Sodium must be kept dry to avoid explosions which may result from evolved hydrogen. When heated it emits toxic fumes of Na_2O . Metallic sodium should be stored in airtight, steel drums. To fight fire use soda ash, dry sodium chloride, powdered talc or graphite. Do not use CCl_4 on fire as an explosion may result.

Electrostatic Sensitivity :

Use in Pyrotechnics : As a fuel and to color burning compositions yellow.

Additional References :

- 1) "Sodium, Its Manufacture, Properties and Uses," M. Sittig, Reinhold Publishing Corp., New York (1956). See especially the chapter on physical and thermodynamic properties.
- 2) "Determination of the Vapor Pressure of Sodium," M. MaKansi et al., J. Phys. Chem. 59, 40 (1955)
- 3) C.A. 37, 2578 (1943)

12, 14, 75,
Addnl. Ref. 3

SODIUM BICARBONATE, NaHCO_3 (Sodium Acid Carbonate, Baking Soda, Sodium Hydrogen Carbonate)			Refs.
Specification No. :	0-S-576B (technical grade)		1,11, 29
Molecular Weight :	84.02		
Crystalline Form :	monoclinic prisms		1
Color :	white		1
Density, g./ml. :	(solid) 2.159-2.22		1
Coefficient of Thermal Expansion :	—		
Heat of Formation, Kcal./mole at 298°K :	(c) -226.5		1
Free Energy of Formation, Kcal./mole at 298°K :	(c) -203.6		1
Entropy, cal./deg./mole at 298°K :	$24.4 \pm .4$		1, 3
See table below			
Melting Point :	loses CO_2 at 543°K (270°C)		1
Heat of Fusion :	—		
Boiling Point :	—		
Heat of Vaporization :	—		
Transition Point :	—		
Heat of Transition :	—		
Heat of Sublimation :	—		

HEAT CONTENT AND ENTROPY OF NaHCO_3
(Base, crystals at 298.15°K)

$T, ^\circ\text{K}$	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	$T, ^\circ\text{K}$	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
350	1140	3.52	400	2320	6.67

$\text{NaHCO}_3(c)$:

Enthalpy : $H_T - H_{298.15} = 10.19T + 18.03 \times 10^{-3}T^2 - 4641$ (0.3 percent ; $298-400^\circ\text{K}$)

Heat Capacity : $C_p = 10.19 + 36.06 \times 10^{-3}T$

Decomposition Temperature: Begins to lose CO_2 at about 50°C , and at 100°C is converted to Na_2CO_3 . In aqueous solution begins to break up into CO_2 and Na_2CO_3 at 20°C and completely on boiling.

Heat of Dissociation, cal./mole : 15,360 Addnl. Ref. 2

Vapor Pressure of dissociation to $(\text{CO}_2 + \text{H}_2\text{O})$ is given by

$$\log P_{\text{mm.}} = 11.185 - \frac{3340.}{T_{\text{abs.}}}$$

Addnl. Ref. 2

See also 42V7

X-Ray Crystallographic Data :

System	Space Group	a	b	c	Axial Angle	Molecules/ Unit Cell	
monoclinic	C_{2h}^2	6.19	6.72	6.49	$\beta = 120^\circ 42'$	4	1

Sodium Bicarbonate, NaHCO_3 (page 2)

gradually loses CO_2 and changes to $\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$

Solubility Data : In water : **6.9 g./100 ml.** at **0°** and **16.4 g./100 ml.** at **60°C**
In alcohol : slightly soluble

Safety Classifications :

OSM :

ICC :

Fire and Explosion Hazard:

Electrostatic Sensitivity :

Use in Pyrotechnics :

inert material

not listed

not listed

none

as a retardant

Additional References :

1) Ref. 52V10

2) R. M. Caven and H. J. Sand, J. Chem. Soc. 99, 1359 (1911)

62

1

SODIUM NITRATE, NaNO_3
(Soda Niter, Chile Niter, Chile Saltpeter, Nitratine, Cubic Niter)

Refs.
1, 11, 12, 29

1'
1
40V2

31
1, 9
1, 9
1, 9

4
4
1
4
4

4

$T, ^\circ\text{K}$	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	$T, ^\circ\text{K}$	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	2495	7.16	579.2 (β) . .	9140	20.59
500	5575	14.01	579.2 (l) . .	12,630	26.62
549.2 (α) . .	7260	17.22	600	13,400	27.93
549.2 (β) . .	8070	18.70	700	17,100	33.63

Heat Capacity: $C_p = 6.34 + 53.32 \times 10^{-3}T$

$\text{NaNO}_3(p)$:

Enthalpy: $H_T - H_{298.15} = 35.701T - 11,536$ (0.1 percent; 549.2-579.2°K)

$\text{NaNO}_3(l)$:

Enthalpy: $H_T - H_{298.15} = 37.00T - 8800$ (0.1 percent; 579.2-700°K)

Heat Capacity, cal./deg./mole : . (solid) 35.70
(liquid) 37.00

4

See also table above

Sodium Nitrate, NaNO₃ (page 2)

Decomposition Temperature :	380°C				1
For DTA and TGA see Refs. 33, 47					
Decomposition Products :	Na ₂ O + NO ₂				33, 47
Vapor Pressure :	—				
X-Ray Crystallographic Data :					
<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>Axial Angle</i>	<i>Molecules/ Unit Cell</i>	
rhombohedral	D _{3h} ⁶	6.3108	α = 47° 15' 59"	2	1, 97V6
at 280°C		6.56	α = 45° 35'		18
hexagonal		5.07	β = 16.829	6	97V6
Hygroscopicity : Deliquesces in moist air. Keep container well closed.					29
Critical R.H. : 82.7% at 20°C (purified material)					32
Gain of purified material (41μ), at 70°F after 120 hours exposure :					33
(at 70% R.H.) 11%					
(90% R.H.) 25.75%					
Water absorbed by 2.000 g. at 25° (40–80 mesh) :					Addnl. Ref. 1
Hrs.	3	5½	7½	16	
g. H ₂ O. absorbed	0.0713	0.1355	0.1970	0.3924	
Solubility Data :					
In water (g./100 xnl.) : 73 at 0°C; 180 at 100°C					12
In NH ₃ :					
In glycerine and acetone :					
very soluble					
slightly soluble					
Health Hazard : Moderately toxic. Large amounts taken internally may be fatal.					93, 12
Safety Classifications :					
OSM : Class 1, packed and stored in original shipping containers.					
Class 2, when not packed or stored in original shipping containers or equivalent.					
ICC : Oxidizing material : yellow label.					
Fire and Explosion Hazard: Sodium nitrate is a dangerous fire and explosion hazard. It can ignite on friction. When heated above 1000°C or when heated with reducing materials, particularly cyanides, it emits toxic fumes on decomposition.					12
Electrostatic Sensitivity :					
Use in Pyrotechnics: As an oxidizer, to impart a yellow color to burning compositions, and incendiary mixtures.					
Additional References :					
1) "Hygroscopic Properties of Sodium, Potassium and Ammonium Nitrates, Potassium Chlorate and Mercury Fulminate," G. B. Taylor and W. C. Cope, Met. & Chem. Eng. 15,141 (1916)					

SODIUM OXALATE

Refs.

Formula : $\text{Na}_2\text{C}_2\text{O}_4$
 Specification No. : **JAN-S-210**
 Specification : The spec. covers one technical grade and three classes based on differences in granulation using U.S. standard sieves.

Class	a	b	c
Through 420 micron (No. 40 sieve) %, min.	99		
Through 250 micron (No. 60 sieve) %, min.		99.9	
Through 149 micron (No. 100 sieve) %, min.			99.9

Molecular Weight :	134.01						
Crystalline Form :	crystalline powder	29					
Color :	white	29					
Density, g./ml. :	(solid) 2.34	1					
Coefficient of Thermal Expansion :	—						
Heat of Formation, Kcal./mole at 298°K :	-314.3	1, 9					
Free Energy of Formation:	—						
Entropy :	—						
Melting Point:	505°K (232-5°C)	1					
Heat of Fusion :	—						
Boiling Point :	—						
Transition Point:	—						
Heat of Sublimation:	—						
Heat Content or Enthalpy :	—						
Heat Capacity, cal./deg./mole :	(solid) 34	9					
Decomposition Temperature, °C :	480	Addnl. Ref. 1					
For DTA see Addnl. Refs. 2, 3							
Decomposition Products :	Na ₂ CO ₃ + CO						
Vapor Pressure:	—						
X-Ray Crystallographic Data :							
System	Space Group	a	b	c	β	Molecules/ Unit Cell	18
monoclinic	C _{2h} ⁵	10.35	5.26	3.46	92° 54'	2	
Hygroscopicity : Spec. grade (20 _μ)							33
Gain in wt. at 70% R.H. and 70°F in 120hr. % :	0.02						
Gain in wt. at 90% R.H. and 70°F in 120hr. % :	0.02						44V21
Material dried at 240°C is not hygroscopic							
Solubility Data: In water at 20°C:	3.7 g./100 g.						1
100°C :	6.33 g./100 g.						
In alcohol:	insoluble						29

Sodium Oxalate (page 2)

Health Hazard : A strong poison. Corrosive and produces local irritation. Taken orally has a caustic effect on the mouth, esophagus and stomach. Can cause severe damage to the kidneys. **12, 29**

Safety Classifications :

OSM : not listed
ICC : not listed

Fire and Explosion Hazard : Dangerous when heated to decomposition : emits toxic fumes **12**

Electrostatic Sensitivity :

Use In Pyrotechnics: As a retardant and to impart a yellow color to burning compositions. **17**

Additional References :

- 1) C.A.48,1891 (1954)
- 2) C.A. 49,14461 (1955)
- 3) C.A. **50,7672** (1956)

SODIUM OXIDE, Na₂O
(Sodium Monoxide)

		<i>Refs.</i>
Specification No. :	—	1
Molecular Weight :	61.99	
Crystalline Form :	deliquesces in air	1
Color :	white	1
Turns yellow on heating		50V12
Density, g./ml. :	(solid) 2.27	1
Coefficient of Thermal Expansion :	—	
Heat of Formation, Kcal./mole at 298°K :	(c)-99.4 ± 1.5	2, 9
See Table a		
Free Energy of Formation, Kcal./mole at 298°K :	(c)-89.9 ± 1.9	2
See Table a		

a. HEAT AND FREE ENERGY OF FORMATION OF Na₂O (c, 1)

T, °K	Δ H (cal./mole)	Δ F° (cal./mole)
298.16. . . .	-99,400 (± 1600)	-89,900 (± 1900)
371	-99,400	-87,500
371	-100,700	-87,500
400	-100,700	-86,500
500	-100,600	-83,000
600	-100,600	-79,400
700	-100,500	-75,900
800	-100,400	-72,400
900	-100,200	-69,000
1000	-99,900	-65,500
1100	-99,500	-62,100
1187	-99,100	-59,100
1187	-145,300	-59,100
1190	-145,300	-58,900
1190	-138,200	-58,900
1200	-138,100	-58,200
1300	-137,100	-51,600
1400	-136,100	-45,100
1500	-135,100	-38,600
1600	-134,100	-32,200
1700	-133,100	-25,900
1800	-132,100	-19,600
1900	-131,100	-13,400
2000	-130,100	-7200

Phase Changes of Metal
M.P. 371°K ; Δ H = 625 cal./g.-atom
B.P., 1187°K ; Δ H = 23,120 cal./g.-atom

Sodium Oxide, Na₂O (page 2)

Entropy, cal./deg./mole at 298°K :	(c) 17.4	9
See Table b		
Melting Point :	1190°K (917°C)	2
Heat of Fusion, cal./mole :	7140	2
Boiling Point :	sublimes at 1548°K (1275°C)	1

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	1750	5.05	800	9350	18.16
500	3600	9.17	900	11,350	20.58
600	5500	12.63	1000	13,500	
700	7400	15.56	1100	15,750	24.93

Na₂O (c) :
 Enthalpy : $H_T - H_{298.15} = 15.70T + 2.70 \times 10^{-5}T^2 - 4921$ (0.7percent ; 298-1100°K)
 Heat Capacity : $C_p = 15.40 + 5.40 \times 10^{-5}T$

Na ₂ O ₂ (c) :		
Heat Capacity : $C_p = 21.35$ (298°K)		
Free Energy Equations :		2
<i>Reaction</i>	<i>Range of Validity, °K</i>	
1) $2 \text{ Na (c)} + \frac{1}{2} \text{ O}_2 \text{ (g)} = \text{Na}_2\text{O (c)}$	298.16-371	
$\Delta F_T^\circ = -99,820 - 7.51T \log T + 5.47 (10^{-5}T^2) - .10 (10^5T^{-1}) + 50.43T$		
2) $2 \text{ Na (l)} + \frac{1}{2} \text{ O}_2 \text{ (g)} = \text{Na}_2\text{O (c)}$	371-1187	
$\Delta F_T^\circ = -100,150 + 4.97T \log T - 2.45 (10^{-5}T^2) - .10 (10^5T^{-1}) + 22.19T$		
3) $2 \text{ Na (g)} + \frac{1}{2} \text{ O}_2 \text{ (g)} = \text{Na}_2\text{O (c)}$	1187-1190	
$\Delta F_T^\circ = -156,280 - 20.72T \log T + 145.48T$		
4) $2 \text{ Na (g)} + \frac{1}{2} \text{ O}_2 \text{ (g)} = \text{Na}_2\text{O (l)}$	1190-2000	
$\Delta F_T^\circ = -150,250 - 23.03T \log T + 147.58T$		
Heat Capacity, cal./deg./mole at 298°K :	(solid) 17.24	
See Table b		
Decomposition Temperature :	above 400°C	Addnl. Refs. 1, 2
Decomposition Products :	Na + O on vaporization	Addnl. Refs. 1, 2
Vapor Pressure (of alkali oxide and alkali metal in equil. with solid alkali oxide) atm. at 1000°K :	(calcd.) 10^{-15}	Addnl. Ref. 3

Sodium Oxide, Na₂O (page 3)

X-Ray Crystallographic Data :

<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>Molecules/Unit Cell</i>
cubic		5.55	

1b

Hygroscopicity : Na₂O reacts vigorously with water with considerable evolution of heat. Keep containers tightly closed.

Solubility Data : In water and alcohol : decomposes
Reacts to neutralize acids.

Health Hazard: Very caustic and dangerous to all tissues. To minimize its effects, wash the area with large volumes of water. Injured person should see a physician.

12

Caution : Do not handle with bare hands. Avoid contact with skin.

M.A.C., mg./m.³ of air : 2

Safety Classifications:

OSM :	not specifically mentioned
ICC :	not specifically mentioned
Alkaline caustic liquids (not otherwise specified)	are classed as corrosive liquids and listed under "Explosives and Other Dangerous Articles."
Coast Guard:	hazardous material
UN:	class 8 (alkaline corrosives)

Fire and Explosion Hazard : Sodium hydroxide formed by the action of water on Na₂O may become a fire hazard when mixed with nitro compounds and other materials. (This hazard must be even greater with powdered, solid Na₂O.)

Electrostatic Sensitivity : ———

Use in Pyrotechnics : Product of the burning of many sodium compounds

Additional References :

- 1) "Sodium, Its Manufacture, Properties and Uses," M. Sittig, Reinhold Publishing Co., New York (1956)
- 2) "The Vapor Pressures of Lithium and Sodium Oxides," L. Brewer and J. Margrave, J. Phys. Chem. **59**, 421 (1956)
- 3) "Stability of Gaseous Alkali and Alkaline Earth Oxides," L. Brewer and D. F. Mastick, J. Am. Chem. Soc. **73**, 2045 (1951)

STEARIC ACID, $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ or $\text{C}_{17}\text{H}_{33}\text{O}_2$
(Octadecanoic Acid, N-Octadecyclic Acid)

Refs.

Specification No. : **MIL-A-271**
 The spec. covers two grades : Grade I in loading ammo. Grade II used as a lubricant, in the pelleting of explosives.
 Molecular Weight : **284.47**
 Crystalline Form : **monoclinic leaflets**
 Color : **colorless**

1

At room temperature stearic acid is a white, fairly hard, wax-like material. It is usually obtained either from fats and oils by hydrolysis and distillation or from oleic acid by hydrogenation. Pearl stearic acid is the material in free flowing powdered bead form for compounding purposes. Stearic acid is also marketed in cakes, powder or flake form, as single, double, or triple-pressed. Successive chillings and pressings remove more of the unsaturated liquid oils (particularly oleic acid), thus raising the melting point and giving a whiter, purer product. Synthetic stearic acid is also made by hydrogenation of unsaturated animal and fish oils.

6.22

Density, g./ml. : **(solid) 847 at 69°C**
 Coefficient of Thermal Expansion, cubical, ~~33.8-44.5°C~~ : **81×10^{-6}**

11

Heat of Formation, Kcal./mole at 18°C,
 at constant press. : **-223.8**
 at constant vol. : **-212.8**

1

~~Free~~ Energy of Formation: **—**

Entropy : **—**

Melting Point : **342.5°K (69.4°C)**
342.7°K (69.6°C)

1

Addnl. Ref. 2

Heat of Fusion, cal./g. : **47.6**

1

Boiling Point : **656°K (383°C)**

1

Transition Point : **—**

Heat of Sublimation : **—**

Heat Content or Enthalpy : **—**

Heat Capacity : **—**

Decomposition Temperature and Products : For DTA see Addnl. Ref. 3

Vapor Pressure, mm. at 60°C : **1.42×10^{-6}**

Addnl. Ref. 1

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	173.9	225.0	263.3	291.0	343.0	370.0d	69.3

1

X-Ray Crystallographic Data :

System	Space Group	a	b	c	Axial Angle	Molecules/ Unit Cell
monoclinic	C_{2h}^4 or C_{2h}^5	5.546	7.381	48.84	$\beta = 63^\circ 38'$	4
		5.68	4.39	50.07	$\beta = 60^\circ$	

1

Addnl. Ref. 2

Hygroscopicity : **—**

Stearic Acid (page 2)

Solubility Data : In water : 0.00029 g./100 g. at 20°C ; 0.034 at 25°C and 0.1 g./ml. at 37°C	1, 29
In alcohol :	2.5 g./100 ml.
In ether :	very soluble
In CHCl ₃ , CCl ₄ , CS ₂ , toluene :	soluble
For additional solvent data see Addnl. Ref. 2	
Health Hazard : Negligible. ~~Used~~ to coat medicinal pills and in face creams.	29
Safety Classifications :	
OSM :	not listed
ICC :	not listed
Fire and Explosion Hazard: Combustible. ~~To fight~~ fire use water, foam, dry chemical, or carbon tetrachloride.	67, 75
Electrostatic Sensitivity :	
Specific Heat, cal./g. at 15°C :	0.399
Liquid at 74–137°C :	0.550
Refractive Index, at 80.2°C :	1.4299
Heat of Combustion, Kcal./mole (H ₂ O liquid)	
at 20°C :	2711.8
Flash Point, °F :	(closed cup) 385 (open cup) 425
Ignition Temperature, °F :	743
Neutralization Value :	197.23
Use in Pyrotechnics:	as a fuel, retardant, binder, and lubricant
Additional References :	
1) "The Vapor Pressure of Some Solid Organic Compounds," R. L. Littlewood, J. Chem. Soc. 1957,2419	
2) "Fatty Acids," K. S. Markley, Ed., Interscience Pub. Co., New York (1960)	
3) J. Phys. Chem. 60 1487 (1956)	
4) E. Médard, Mém. artillerie franç. 28,465 (1954)	

STRONTIUM CHLORIDE, SrCl₂

Refs.

Specification No. :	---	
Molecular Weight :	158.54	
Crystalline Form :	cubic	1A
Color :	colorless	1A
Density, g./ml. :	(solid) 3.052	1A
(liquid) $D_t = 2.69 - 0.00045 \text{ (to } 900^\circ\text{C)}$		
Temp. °C	900	950
	1000	1050
Density	2.69	2.67
	2.645	2.62
Coefficient of Thermal Expansion, cubic at 870°C :	166×10^{-6}	44829
Heat of Formation, Kcal./mole at 298°K :	(c) -198.0	9,248
Free Energy of Formation, Kcal./mole at 298°K :	(c) -186.7	9
	-187.5	6
Entropy, cal./deg./mole at 298°K :	28	9,318
	31.7	6
Melting Point, °C :	873	1A, 24A
	875	41
Heat of Fusion, Kcal./mole at 1148°K (875°C) :	4.2	44S29
	4.1	9, 41, 6
	4.1 ± 0.6	24A
Boiling Point, °C :	1300	44329
	1250	52
Heat of Vaporization, Kcal./mole :	55	6
Transition Point :	---	
Heat of Sublimation :	---	
Heat Content or Enthalpy :	---	
Heat Capacity, cal./deg./mole :	(solid) 18.9	9
$C_p = 18.20 + 2.45 \times 10^{-3} \text{ (est'd over } 298 - 1145^\circ\text{K)}$		4
See also Ref. 24A		
Decomposition Temperature : Noticeable above approx. 955°C		44829
Heating in air or O ₂ at red heat slowly changes the chloride to the oxide		52V11, 54V3
Decomposition Products :	---	
Vapor Pressure :	---	
X-Ray Crystallographic Data :		
System	Space Group	<i>a</i>
cubic	O _h ³	6.9767
		Molecules/Unit Cell
		97V4
Hygroscopicity :	hygroscopic	44829
	very hygroscopic	52V11

Strontium Chloride, SrCl₂ (page 2)

Solubility Data : In H ₂ O, g./100 ml. 43.5 at 0°C and 100.8 at 100°C	1A
In absolute alcohol, acetic acid :	very slightly soluble
In NH ₃ :	insoluble
Health Hazard : Probably slight. The Sr ion has a low order of toxicity.	12
Safety Classifications:	
OSM :	not listed
ICC :	not listed
Fire and Explosion Hazard:	—
Electrostatic Sensitivity :	—
Use in pyrotechnics :	to color burning compositions crimson

Refs.

Specification No. :	MIL-S-20322			
The spec. covers one grade and three classes which differ in granulation.				
Molecular Weight :	211.65			
Crystalline Form :	cubic			
Color :	colorless			
Density, g./ml. :	(solid) 2.986			
Coefficient of Thermal Expansion, linear, 30-75°C :	$\alpha = 3.22 \times 10^{-5}$	44S29 sup		
Heat of Formation, Kcal./mole at 298°K :	-233.25	1, 9		
Free Energy of Formation, Kcal./mole at 298.16°K :	-185.8	B6		
Entropy, cal./mole at 298.16°K :	47.4	86		
Melting Point :	918°K (645°C) 891°K (618°C)	9 47		
Heat of Fusion:	—			
Boiling Point :	decomposes 580-600°C	Addnl. Ref. 1		
Transition Point :	—			
Heat of Sublimation :	—			
Heat Content or Enthalpy :	—			
Heat Capacity, cal./deg./mole :	(solid) 38.3 (290-320°K)	4		
Decomposition Temperature, °C :	580-600	Addnl. Ref. 1		
For DTA and TGA see Ref. 33				
Vigorous bubbling at 672°C		47		
Decomposition Products :	SrO + NO ₂ ; toxic fumes emitted	47		
Vapor Pressure :	—			
X-Ray Crystallographic Data :				
System	Space Group	a	Molecules/Unit Cell	
cubic	T _h ⁸	7.81	4	1
Hygroscopicity (gain, mg./g., at R.T. after equilibrium has been established in a vacuum desiccator) :				32
	65	75	86	93
% , R.H.	24 hr. equil.	24 hr. equil.	24 hr. equil.	24 hr. equil.
Purified	0.3	0.3	s	—
Spec. grade	0.3	0.1	—	312.6
	<.1	0.2	s	—
Critical R.H. :			purified 82.7% at 20°C spec. grade 82.9% at 26.2°C	
Solubility Data : In water (g./100 ml.)	40.1 at 0°	and 100 at 90°C		1
In abs. alcohol, NH ₃ :		very slightly soluble		
In acetone :		slightly soluble		

Strontium Nitrate, $\text{Sr}(\text{NO}_3)_2$ (page 2)

Health Hazard : Moderately toxic. Large amounts taken by mouth **may** have fatal effects. $\text{Sr}(\text{NO}_3)_2$ emits toxic fumes on decomposition. **93, 12**

Safety Classifications:

OSM : **Class 1**, in original containers.

Class **2** when not packed or stored in original shipping containers or equivalent.

ICC : Oxidizing material ; yellow label.

Fire and Explosion Hazard : A fire and explosion hazard. **As** an oxidizer it can give up its oxygen to other materials to produce **a** vigorous reaction which may result in detonation. Toxic fumes are emitted on decomposition. **12, 14**

Electrostatic Sensitivity :

Use in Pyrotechnics: An oxidizer and to impart **a** crimson color to burning compositions. (Nonhygroscopic strontium nitrate is used in tracer and pyrotechnic compositions that are sensitive to deterioration by moisture.) **17**

Additional References :

- 1) C.A.S9,12932 (1955)

STRONTIUM OXALATE ANHYDROUS AND MONOHYDRATE,
 SrC_2O_4 and $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$

Refs.

Specification No. : MIL-S-12210

The spec. covers both the anhydrous salt and the monohydrate : Grade A, anhydrous, and Grade B, hydrated. The two grades differ also in granulation.

Molecular Weight : (anhydrous) 183.65
(monohydrate) 193.67

Crystalline Form : —

Color : colorless

1

Density, g./ml. : —

Heat of Formation, Kcal./mole at 18°C, anhydrous :

at constant press. : -327.7

at constant vol. : -326.5

Addnl. Ref. 1

Free Energy of Formation, Kcal./mole at 18°C, monohydrate :

(c) 360.8

1

Entropy : —

Melting Point : See Decomposition Temperature below

Heat of Fusion : —

Boiling Point : —

Transition Point : —

Heat of Sublimation : —

Heat Content or Enthalpy : —

Heat Capacity : —

Decomposition Temperature: TGA. The hydrate begins to lose H_2O at 43°C.

Addnl. Ref. 2

All the water is off by 177°C. On further heating the weight remains constant up to around 400°C.

Decomposition Products: Dissociates into SrCO_3 and dangerous CO over the range 400-520°C.

Addnl. Ref. 2

See graph below

Vapor Pressure : —

X-Ray Crystallographic Data for $\text{SrC}_2\text{O}_4 \cdot 2\frac{1}{2} \text{H}_2\text{O}$

Sym- metrical	space Group	a	b	c	Molecules/Unit Cell
tetragonal	C_{4h}	12.795	7.509		18V2

18V2

Hygroscopicity : —

Solubility Data: For $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, required for solution of 1 part: 2000 parts of water, 1900 parts of 3.5% acetic acid, 1115 parts of 23% acetic acid, least soluble in 35% acetic acid. Readily soluble in dilute HCl or HNO_3 .

29

1

Health hazard: Highly toxic. Corrosive and produces local irritation. When taken orally may have a caustic effect on the mouth, esophagus and stomach.

12

93

Safety Classifications :

OSHA : not listed

ICC : not listed

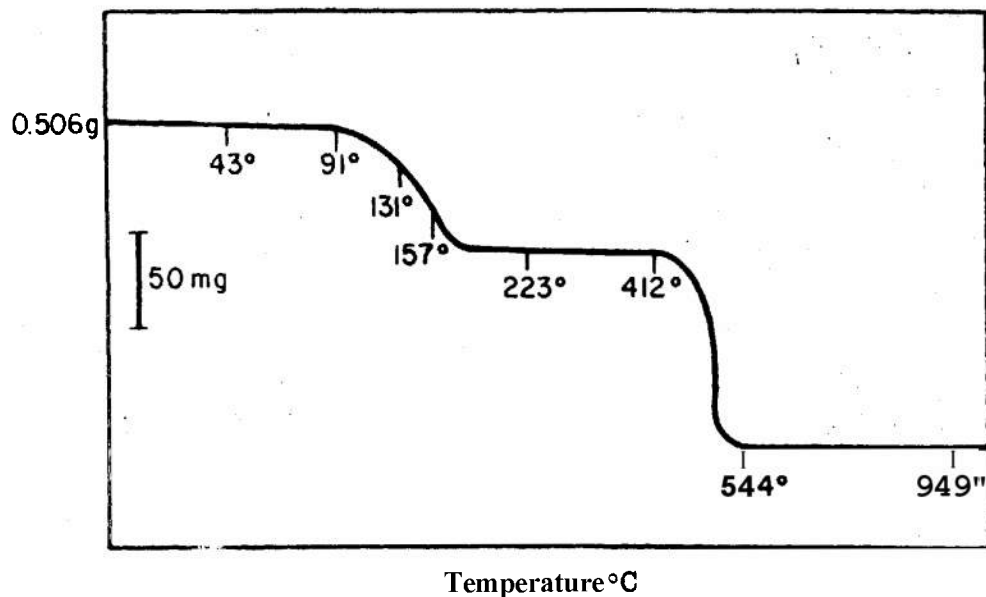
Strontium Oxalate Anhydrous and Monohydrate (page 2)

Fire and Explosion Hazard: Dangerous when heated to decomposition. Emits poisonous carbon monoxide. 12

Electrostatic Sensitivity :

Use in Pyrotechnics: SrC_2O_4 and $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ are used as retardants and to impart a scarlet color to burning compositions. 17

PYROLYSIS OF $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$



Additional Ref. 2

Additional References :

- 1) L. Mécand, Mém artillerie franç. 28, 467 (1954)
- 2) S. Pelletier and C. Duval, Anal. Chem. Acta. 1, 358 (1947)

STRONTIUM PERCHLORATE, $\text{Sr}(\text{ClO}_4)_2$

Refs.

Specification No. :	—	
Molecular Weight :	286.54	
Percent Oxygen :	44.67	
Crystalline Form :	—	
Color :	colorless	1
Density, g./ml. :	—	
Coefficient of Thermal Expansion :	—	
Heat of Formation, Kcal./mole at 298°K :	-184 (estd.)	12
Free Energy of Formation, :	—	
Entropy :	—	
Melting Point :	—	
Heat of Fusion :	—	
Boiling Point :	—	
Transition Point :	—	
Heat of Sublimation :	—	
Heat Content or Enthalpy :	—	
Heat Capacity :	—	
Decomposition Temperature : Vigorous decomposition at 477°C. For DTA and TGA see Ref. 33		47
Decomposition Products :	—	
Vapor Pressure :	—	
X-Ray Crystallographic Data :	—	
Hygroscopicity :	—	
Solubility Data: In water, 310 g./100 ml. at 25°C; very soluble in hot water		1
Solubility in Organic Solvents at 25°C :		
<i>Solvent</i>	<i>g./100 g. solvent</i>	72, 77
Methyl alcohol	212.01	
Ethyl alcohol	180.66	
Acetone	150.06	
Ethyl acetate	136.93	
Ethyl ether	insoluble	
Health Hazard: Avoid contact. Irritating to skin and mucous membrane.		12
Safety Classifications :		
OSM : Class 1, Class 2 when not packed or stored in original shipping containers or equivalent.		
ICC: Oxidizing material ; yellow label. Listed under "Explosives and Other Dangerous Articles."		
Fire and Explosion Hazard : Can be exploded by shock, heat, or chemical action. It is a explosive hazard when mixed with carbonaceous materials, finely divided metals, or sulfur. It emits highly toxic fumes. Fires involving the perchlorate alone may be fought with water.		12, 14
Use in Pyrotechnics: As an oxidizer and to impart a scarlet color to burning compositions.		

STRONTIUM PEROXIDE, SrO_2		Refs.
Percent Oxygen :	26.75	
Specification No. :	JAN-S-612	
Covers two grades that differ in purity and granulation.		
Molecular Weight :	119.63	
Crystalline Form :	powder	1
Color :	white	
Density, g./ml. :	(solid) 4.56	1
Coefficient of Thermal Expansion :	—	
Heat of Formation, Kcal./mole at 298°K :	-153.6	1, 9
See table below		
Free Energy of Formation, Kcal./mole at 298°K :	-141	2
See table below		
HEAT AND FREE ENERGY OF FORMATION OF $\text{SrO}_2(\text{c})$		4
T, °K	A H (cal./mole)	A F° (cal./mole)
298.16	-153,500 (± 5000)	-141,000 (± 6000)
400	-153,000	-137,000
500	-153,000	-133,008
600	-152,500	-129,000
700	-152,000	-125,000
800	-151,500	-121,500
900	-151,000	-117,500
1000	-150,500	-114,000
Free Energy Equation :		
$\text{Sr (c)} + \text{O}_2 \text{ (g)} = \text{SrO}_2 \text{ (c)}$		
$\Delta F^\circ = -155,510 - 11.40T \log T + .305 (10^{-3}T^2) + .675 (10^{-5}T^3) + 75.44T$		
Reaction Range of Validity, °K 298.16-1000		
Entropy, cal./deg./mole at 298°K :	14.8	6
For calculation see thermodynamic equation in Ref. 2		
Melting Point :	decomposes at 488°K (215°C)	6, 8
Heat of Fusion :	—	
Boiling Point :	—	
Transition Point :	—	
Heat of Sublimation :	—	
Heat Content or Enthalpy:		
For calculation see thermodynamic equation in Ref. 2		
Heat Capacity :		
For calculation see thermodynamic equation in Ref. 2		

Strontium Peroxide, SrO₂ (page 2)

Decomposition Temperature :

dissociates at

357°C

480°C

410°C and TGA

Addnl. Ref. 2

Addnl. Ref. 3

Addnl. Ref. 4

Decomposition Products :

Vapor Pressure: Dissociation Pressure between 322 and 800° is given by

$$P_{\text{atm}} = -\frac{20280}{4.5711T} - 0.010T + 1.75T + 2.8$$

Addnl. Ref.

1

Addnl. Ref. 2

Addnl. Ref. 2

97V6

29

32

31% R.H.	43% R.H.	52% R.H.	65% R.H.
24 hr. equil.	24 hr. equil.	24 hr. equil.	24 hr. equil.
0.4 4.5	0.6 2.2	2.3 21.4	84.3 178.3 56.3 136.0
75% R.H.	86% R.H.	93% R.H.	
24 hr. equil.	24 hr. equil.	24 hr. equil.	
210.5 474.7 161.0 356.0	418.4 S 251.0 682.0	S S 354.0 834.0	

Strontium Peroxide, SrO_2 (page 3)

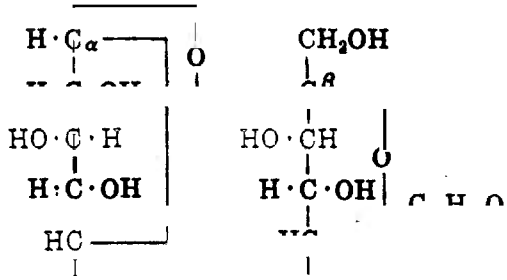
Fire and Explosion Hazard : Heat, **shock**, or catalysts may cause violent decomposition. Reacts violently when heated with reducing materials. Contact with water produces heat. **12, 14**

Electrostatic Sensitivity : **17**

Use in Pyrotechnics : As an oxidizer to impart a red color to burning compositions.

Additional References :

- 1) "Direct Oxidation under High Pressures. The Oxides of Strontium, Barium, Lead, Manganese and Cobalt," C. B. Holtermann, Ann. Chim. **24, 121 (1940). C.A. 35, 7859 (1941)**
- 2) "On the Formation and Dissociation of Strontium Peroxide," C. Holtermann and P. Lafitte, **Compt. rend. 208, 617 (1939). C.A. 33, 2833 (1939)**
- 3) "Heating Curves for the Hydrates of the Peroxides of Group II Metals," I. I. Vol'nov, C.A. **52, 19384 (1958)**
- 4) "Thermography of Peroxide Compounds," I. I. Vol'nov, **C.A. 48, 7416 (1954)**

SUGAR		Refs.
(Cane Sugar, Sucrose, Saccharose, (α -D-glucosido)- β -D-fructofuranoside α -D-glucopyranosido- β -D-fructofuranoside)		1 29
Formula :		Addnl. Ref. 5
Specification No. :	CH ₂ OH CH ₂ OH JJJ-S-00791C	
The specification covers two types of beet or cane sugar. Type 1 : white hard, refined (a) granulated or (b) powdered ; and Type 2 : brown, soft (a) light (b) medium and (c) dark. Type 1 granulated is used for pyro techniques.		
Molecular Weight :	342.30	
Crystalline, Form :	needles (from alcohol), monoclinic	1, 29
For crystallography see Addnl. Ref. 3 Sucrose crystals are triboluminescent.		
Color :	white	1
Density, g./ml. at 15°C :	crystallized, 1.5879 powdered, 1.5897	Addnl. Ref. 3v1
Coefficient of Thermal Expansion, linear for		Addnl. Ref. 3V1
longest axis :	28×10^{-4}	
width :	50×10^{-4}	
shortest :	29×10^{-4}	
cubical (calculated) :	1.1×10^{-4}	
Heat of Formation, Kcal./mole at 18°C :	H _p = -536.5 H _v = -527	Addnl. Ref. 1
Free Energy of Formation :	—	
Entropy, cal./deg./mole at 298°K :	86.1	Addnl. Ref. 3V1
Melting Point (when crystallized from alcohol) :	461°K (188°C, decomp.) 458 (185-6°C)	1 Addnl. Ref. 3v1
When sucrose is heated cautiously to the melting point (185-186°C) it forms a viscous, colorless melt ;however, when heated longer or to a higher temperature decomposition takes place.		
Heat of Fusion, Kcal./mole :	(decomposes) 4.6	Addnl. Ref. 3v1

Sugar (page 2)

Boiling Point:	decomposes							Addnl. Ref. 3V1
Transition Point:	—							
Heat of Sublimation:	—							
Heat Content or Enthalpy:	—							
Heat Capacity:	—							
Molar Heat and Specific Heat of Crystallized Sucrose:								
Temp. °C	0	20	40	60	80	90		
C _p (cal./mole)	92.1	99.3	108	116	125	129		
C _p (cal./g.)	0.260	0.290	0.316	0.339	0.366	0.377		
Decomposition Temperature, °C:								29
Decomposition Products: Loses water, caramelizes, and then chars when heated above its melting point.								29, 50
For DTA see Addnl. Ref. 4								
Vapor Pressure:								—
X-Ray Crystallographic Data:								
System	Space Group	a	b	c	Axial Angle	Molecules/ Unit Cell	18	
monoclinic	C ₂	10.89	8.69	7.77	103°	2	85	
Hygroscopicity: Powdered sugar absorbs up to 1% moisture in air, which is given up on heating at 90°C.								29
Solubility of Sucrose in Water:								
Temp. °C	0	20	40	60	80	90	100	
g./100 g. H ₂ O	179.2	203.9	238.1	287.3	362.2	415.7	487.2	
Solubility: In alcohol and methanol ca. 1g./100 ml. Moderate sol glycerol and pyridine. Sol ether common organic solvents. Insoluble in gasoline, CHCl ₃ , CCl ₄ , turpentine. Noticeably soluble in aniline, ethyl acetate, and amyl acetate.								1 29 Addnl. Ref. 3 98
Health Hazard:								nontoxic
Safety Classification:								not listed
Fire and Explosion Hazard.								
Autoignition Temperature, °C:								385
Electrostatic Sensitivity:								—
Specific Heat, cal./15°g./°C at 20°C:								0.299
Optical Rotation: $\alpha \frac{25}{D}$ (26 g. in 100 ml. H ₂ O, 2 dm tube) +66.47 to 66.49 depending on the solvent from which it is crystallized.								29
Heat of Combustion, Kcal./mole:								1351.3
Kcal./g.:								3,949
Use in Pyrotechnics:								as a fuel
								50

Sugar (page 3)

Additional References:

- 1) L. Médard, *Mém artillerie franç* 28,481 (1954)
- 2) "On Saccharose B," A. Pictet and H. Vogel, *Helv. Chim. Acta* 11, 901 (1928)
- 3) "Principles of Sugar Technology," P. Honig, Ed., Vol. 1, Elsevier Publishing Co., New York (1953)
- 4) "Differential Thermal Analysis of Organic Compounds," A. T. Perkins and H. L. Mitchell, *Transactions of The Kansas Academy of Science* 60, No. 4 pp. 437-40 (1967)
- 5) "X-Ray Examination of Sucrose," C. A. Beeves and W. Cochran, *Nature* 157,872 (1946)

SULFUR (SULPHUR), S₈
(Flowers of Sulfur, Milk of Sulfur, Brimstone)

Refs.

Specification No. : JAN-S-487

The specification covers five grades of ground S:

A, ground crude S used for black powder.

B, ground crude S used for pyrotechnics compositions.

C, ground crude S used for pyrotechnics compositions.

D, ground refined S used for nongaseous **powders** and primer compositions.

E, ground crude S used **for** pyrotechnic compositions. The grades differ slightly in purity and in granulation.

Molecular Weight : 256.53

Crystalline Form : (α) rhombic, (β) monoclinic, (γ) amorphous

1, 46

Color : yellow

Forms of Sulfur: Solid sulfur (S) exists in two crystalline forms, rhombic and monoclinic, and also as an elastomer. The rhombic form is stable at ordinary temperatures. Above the transition temperature of 95.4°C and up to the boiling point monoclinic S is the stable variety. Elastic S is prepared by rapidly chilling liquid S which has been heated to elevated temperatures. The infrared spectrum is identical with that of liquid S. On melting, S becomes a straw-yellow transparent liquid, designated as λ S. The liquid may be supercooled in bulk far below its freezing point to room temperature in the form of droplets **which** in time may solidify to a clear yellow glass. At about 160°C, the liquid is dark brown. Its color deepens **as** the temperature is raised, **and** above 250°C, it turns brownish-black. Apparently the structure of the liquid undergoes an abrupt change at about 160°, and this transformation is accompanied by the absorption of 2.751 cal./g. The sudden and enormous increase in viscosity which occurs at this temperature is one indication of a structural alteration. Other properties **show** a marked discontinuity. Long chain polymers referred to as μ S, in equilibrium with rings of octatomic molecules, apparently exist in the liquid above 160°. Beyond 230° the viscosity decreases but the color remains dark up to the boiling point, 444.6°C. **If** S at the boiling point is cooled **slowly**, it passes through the changes described above in the reverse order.

46

"**Flowers**" of sulfur is a term applied to the mined molten S which is finely ground. It is the type used for pyrotechnic purposes.

20V3

Density, g./ml. : (solid) rhombic 2.07
monoclinic 1.96
amorphous 1.92

1, 46

Coefficient of Thermal Expansion :

46

Temp. °C	Linear (rhombic)	Cubic (rhombic)
6-13	4.567×10^{-5}	13.70×10^{-5}
13-50	7.433×10^{-5}	22.30×10^{-5}
50-78	8.633×10^{-5}	25.90×10^{-5}
78-97	20.67×10^{-5}	62.01×10^{-5}
97-110	103.2×10^{-5}	309.6×10^{-5}

Sulfur (Sulphur) S₈ (page 2)

Heat of Formation, Kcal./mole at 298°K :	(gas) 53.25	1, 9
Free Energy of Formation, Kcal./mole at 298°K :	(gas) 43.57	9
Entropy, cal./deg./mole at 298°K :	(rhombic) 7.62	5, 9
	(monoclinic) 7.78	5, 9

See Tables a, b, c, d

Melting Point, °C: (α) 112.8(β) 119.25(γ) about 120		1
Heat of Fusion, cal./g. :	(rhombic) 11.9	9
	(monoclinic) 9.2	

Boiling Point, °C:	444.6	1, 46

Heat of Vaporization, cal./mole at 717.75°K :	2300	5

Transition Point, °C :		
(rhombic → monoclinic)	95.4	46
(liquid → +viscous)	159.9	46

Heat of Transition, cal./g.:		
(rhombic to monoclinic)	2.992	46
(liquid to viscous)	2.751	

Heat of Sublimation, cal./mole at 298°K :	S ₈ 24,350	5
	S ₂ 330,840	

Heat Content or Enthalpy, cal./mole at 298°K :	(solid) 1053	5

See Tables a, b, c, and d

a. **HEAT CONTENT AND ENTROPY OF S** (c, 1) (Base, rh-crystals at 298.15°K)

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
353	290	0.90
368.6 (rh)	400	1.20
368.6 (mon)	485	1.43
392 (mon)	630	1.82
392 (l)	965	2.67
400	1030	2.83
500	1940	4.85
600	2780	6.38
700	3650	7.72
717.8	3810	7.95

S (rh) :

Enthalpy : $H_T - H_{298.15} = 3.58T + 3.12 \times 10^{-3}T^2 - 1345$ (0.2 percent ; 298-368.6°K)

Heat Capacity : $C_p = 3.58 + 6.24 \times 10^{-3}T$; $H_{368.6} = 85$

S (mon) :

Enthalpy : $H_T - H_{298.15} = 6.20T - 1800$ (0.1 percent ; 368.6-392°K)

Heat Capacity : $C_p = 6.20$; H_{392} (fusion) = 335

S (l) :

Enthalpy : $H_T - H_{298.15} = 8.73T - 2457$ (0.6 percent ; 392-717.8°K)

Heat Capacity : $C_p = 8.73$

Sulfur (Sulphur) S₈ (page 3)

b. HEAT CONTENT AND ENTROPY OF S (g)

(Base, ideal gas at 298.15°K)

4

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	570	1.65	1900	8320	9.79
500	1120	2.88	2000	8830	10.06
600	1660	3.86	2200	9850	10.54
700	2190	4.68	2400	10,875	10.99
800	2715	5.38	2600	11,910	11.40
900	3235	5.99	2800	12,950	11.79
1000	3750	6.53	3000	13,995	12.15
1100	4260	7.02	3500	16,650	12.96
1200	4770	7.46	4000	19,340	13.68
1300	5280	7.87	4500	22,065	14.32
1400	5790	8.25	5000	24,810	14.90
1500	6295	8.60	6000	30,330	15.91
1600	6800	8.92	7000	35,860	16.76
1700	7305	9.23	8000	41,390	17.50
1800	7815	9.52			

S (g) :

Enthalpy: $H_T - H_{298.15} = 5.26T - 0.05 \times 10^{-3}T^2 - 0.36 \times 10^5T^{-1} - 1443$
(0.6 percent; 298-2400°K)Heat Capacity: $C_p = 5.26 - 0.10 \times 10^{-3}T + 0.36 \times 10^5T^{-2}$ Enthalpy: $H_T - H_{298.15} = 4.96T + 0.05 \times 10^{-3}T^2 - 0.60 \times 10^5T^{-1} - 1282$
(0.2 percent; 2400-8000°K)Heat Capacity: $C_p = 4.96 + 0.10 \times 10^{-3}T + 0.60 \times 10^5T^{-2}$ c. HEAT CONTENT AND ENTROPY OF S₂ (g)

(Base, ideal gas at 298.15°K)

4

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	810	2.34	1500	10,430	13.79
500	1640	4.18	1600	11,325	14.37
600	2485	5.72	1700	12,225	14.91
700	3345	7.05	1800	13,125	15.43
800	4220	8.22	1900	14,025	15.92
900	5095	9.25	2000	14,925	16.38
1000	5975	10.17	2200	16,730	17.24
1100	6855	11.01	2400	18,545	18.03
1200	7745	11.79	2600	20,360	18.76
1300	8635	12.50	2800	22,175	19.43
1400	9535	13.17	3000	23,995	20.06

Sulfur (Sulphur) S₈ (page 4)H_{298.15}

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg.
400	3935	11.32	800	20,580	40.06
500	7985	20.37	900	24,850	45.09
600	12,125	27.90	1000	29,140	49.62
700	16,330	34.39			

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	183.8	243.8	288.3	327.2	399.6	444.6	112.8

Form	Range	Equation (P in mm., T in °K)
rhombic	20-80	$\log P = 11.664 - \frac{5166}{T}$
monoclinic	96-116	$\log P = 11.364 - \frac{5082}{T}$
liquid	25-74	$\log P = 8.70 - \frac{4055}{T}$
	120-325	$\log P = 14.7000 - .0062238T - \frac{5405.1}{T}$
	325-550	$\log P = 7.43287 - \frac{3268.2}{T}$

X-Ray Crystallographic Data:

System	Space Group	a	b	c	Atoms/ Unit Cell
rhombic	V _h ²⁴	10.37	12.845	24.369	128 (16 eight-membered rings)
monoclinic	C _{2h}	10.90	10.96	11.02	48 (6 eight-membered rings)

Hygroscopicity:

Spec. grade, % gain at 70°F in 168 hr. :

none at 40, 50, and
70% R.H.
0.01 at 90% R.H.

Sulfur (Sulphur) **Sl @age 5)**

Solubility Data :

In water :	insoluble	20
In alcohol and ether :	slightly soluble	
In carbon disulphide, 70 g./100 g. :	soluble	
In light petroleum, hot benzene, toluene and benzyl chloride :	soluble	46

Health Hazard : Believed to be nontoxic. Tank car shipments of molten sulfur may accumulate poisonous H_2S gas, which is also flammable and explosive. In unloading operations suitable precautions should be taken. **93, 46**

Safety Classifications :

OSM :	not specified
Probably class 2 as a pyrotechnic material.	
ICC :	not mentioned
U.N.	an inflammable solid
Coast Guard:	hazardous

Fire and Explosion Hazard : When ignited, molten **S** will burn in air producing acid fumes of SO_2 , which are irritating, suffocating and lachrymatory, and inhalation should be avoided. Burning **S** can react vigorously with oxidizing materials. Sulfur when compounded with chlorates and some other oxidizing agents, forms sensitive explosive mixtures. When mixed with carbon, lampblack, fats and oils, **S forms** mixtures which can ignite spontaneously. It should be stored away from oxidizing agents. To fight fire use water. **12, 14, 46, 75**

Electrostatic Sensitivity : When **rubbed** with most substances it becomes negatively charged.

Minimum energy required for ignition by an electric spark, millijoules : **26**

Ignition Temperature, in air at atmospheric pressure, $^{\circ}C$: **46**

	15	
closed cup :	248-261	
	405$^{\circ}F$	75
open cup :	440$^{\circ}F$	

Minimum Explosive Concentration of dust, mg./l. : **26**
22

Heat of Combustion, Kcal./g. : **1**
(monoclinic) 2.240
(rhombic) 2.200

Additional References :

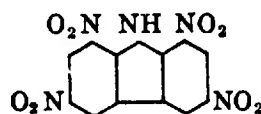
- 1) "The Sulphur Data Book," W. N. Tuller, Ed., McGraw-Hill Book Co., New York (1954)
- 2) "The National Fire Codes, Vol. II, Combustible Solids, Dusts, Chemicals and Explosives," National Fire Protection Association, Inc., Boston, Mass. (1958)
- 3) "The National Fire Codes, Vol. II, The Prevention of Dust Explosions," National Fire Protection Association, Inc., Boston, Mass. (1952)
- 4) "Sulfur May Have Helical Structure," **C & EN**, p. 44 (Sept. 5, 1960)
- 5) Trans. Faraday Soc. 55, No. 444, 2221 (1959)

TETRANITROCARBAZOLE, (C₆H₂)₂ (NO₂)₄NH
(Tetranitrobenzopyrrole, Tetranitroidiphenylamine, TNC)

Specification No. : **PAPD-639 (1954)** pending revision of **MIL-T-13723**
Molecular Weight : 347.20

Crystalline Forms : α , needles ; β , plates ; γ (1,3,6,8) prisms
Color : light yellow

TNC is produced by treating carbazole with sulphuric acid and then nitrating the sulphonic acids to yield a mixture of principally 1,3,6,8 and about 10% of 1,2,6,8 TNC. The structure of the 1,3,6,8 isomer is



Density, g./ml. : _____

Coefficient of Thermal Expansion : _____

Heat of Formation : _____

Free Energy of Formation: _____

Entropy: _____

Melting Point,

α : about 581°K (308°C)
with decomposition
 β : 593°K (320°C)
 γ : (1,3,6,8) 558°K
(285°C) with
decomposition

Specification : 285°C min. to 300°C max.

Boiling Point : _____

Transition Point : _____

Heat of Sublimation : _____

Heat Content or Enthalpy: _____

Heat Capacity : _____

Decomposition Temperature : Decomposes
on heating :

turns red-brown above
200°C

For DTA see Ref. 33

Decomposition Products : _____

Vapor Pressure : _____

X-Ray Crystallographic Data : _____

Hygroscopicity, at 30°C, 90% R.H. :

0.01

Refs.

13

1B

88V20

Addnl. Ref. 1

88V20

Addnl. Ref.

13

Tetranitrocarbazole, (C₆H₂)₂(NO₂)₄NH (page 2)

Solubility Data : In water (g./100 g.) at 95°C :	0.1	13, Addnl. Ref. 3
In nitrobenzene :	very soluble	
In hot acetone and hot pyridine :	soluble	
In nitrobenzene, chloroform, CCl ₄ , ether., ligroin :	insoluble	
α—in glacial acetic acid :	practically insoluble	88V20, Addnl. Ref. 2
in KOH :	soluble with formation of a yellow color	
in conc. H ₂ SO ₄ :	soluble with formation of a green color	
p—in glacial acetic acid (hot) :	soluble	
γ—in glacial acetic acid :	3.05%	
in pyridine :	3.55%	
in ethyl alcohol :	trace	
Health Hazard :	toxic ; and is used as an insecticide	12
Safety Classifications :		
OSM :	class 9	
ICC :	not listed	
Fire and Explosion Hazard: Dangerous, exploded by shock. When heated to decomposition it emits highly toxic fumes. Can react vigorously with oxidizing materials.		12
Electrostatic Sensitivity :	—	
Data on γ (1,3,6,8) TNC		13
Oxygen Balance to CO ₂ , % :	-85	
Oxygen Balance to CO, % :	-30	
Nitrogen (calc'd for C.P.) % :	20.0	
Nitro nitrogen (calc'd for C.P.) % :	16.0 (spec. min. 15.5)	
M.P., °C :	296	
Impact Sensitivity : 2 kg. wt., sample weight 14 mg. :		
B.M. apparatus, cm. :	100+	13
P.A., in. :	18	
Friction Pendulum Test :	unaffected by fibre or steel shoe	
Explosion Temperature (5sec.), °C :	decomposes at 470	
100°C Heat Test:		
% loss first 48 hrs.:	0.15	
% loss second 48 hrs.:	0.05	
Explosion in 100 hrs.:	none	
Vacuum Stability Test, cc. gas/40 hrs. from a 5 g. sample :		
100°C:	0.2	
120°C:	0.2	
Sand Test (200g. bomb)		
Sand crushed through 30 mesh screen :	(gas) 41.3	

Tetranitrocarbazole, $(C_6H_2)_2(NO_2)_4NH$ (page 3)

Sensitivity to Initiation :

Lead Azide **8.20 g.** plus tetryl 0.25g.

Method of Loading:

pressed

Method of Storage:

dry

Heat of Combustion, cal./g. at 18°C:

3772.4

Addnl. Ref. 3

Use in Pyrotechnics:

as a fuel, particularly in
some igniter powders

Additional References:

- 1) "Identification of Isomers **Formed** in the Nitration of Carbazole," D. B. Murphy et al., J. Am. Chem. Soc. **75,4289 (1953)**
- 2) CA **48,2084 (1954)**
- 3) Picattiny Arsenal Technical Reports **1647,1802,1937,1973, 1984, and 2180**
- 4) P. Tavernier and Maurice Lamoroux, Mem. Poudres **89,341 (1957)**
- 5) "Über die Einwirkung von Athylnitrat auf Diphenyl und Diphenyl. Abkömmlinge," H. Raudnitz, Ber. **60,741 (1927)**

"THIOKOL" (LIQUID POLYMER LP-2)

(Thiokol is a trademarked name)

Thiokol **LP-2 Mix** is a polymer manufactured by the Thiokol Corporation in the liquid state. It is a completely polymerizable material which can be converted by suitable curatives to a tough resilient rubber without appreciable shrinkage. In the rubber state it remains flexible to **-65°F** and does not melt at elevated temperatures. Its maximum service temperature is around **250°F**, but it will stand higher intermittent temperatures. It **is** sold as a viscous liquid with a viscosity of about **400** poises at **25°C**. It is cold setting.

Formula or Structure: The average structure is as follows:

$\text{HS}-(\text{C}_2\text{H}_4-\text{CH}_2-\text{O}-\text{C}_2\text{H}_4-\text{S}-\text{S})_{23}-\text{C}_2\text{H}_4-\text{O}-\text{CH}_2-\text{O}-\text{C}_2\text{H}_4-\text{SH}$. Occasionally in the chain of recurring units there is a side mercaptan group. The terminal SH groups are very reactive.

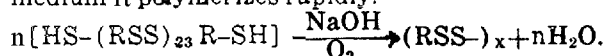
Specifications:

none

Physical Properties :

Color:	amber
Specific Gravity:	1.27
Molecular Weight:	approximately 4000
Stability:	indefinite
Moisture Control	less than 0.2%
pH (of water extract)	6.0 to 8.0

Chemical Reactivity : LP-2 is slightly acid when pure and is stable. In alkaline medium it polymerizes rapidly.



The reaction is exothermic. R in the above equation denotes the group $(\text{C}_2\text{H}_4-\text{O}-\text{CH}_2-\text{O}-\text{C}_2\text{H}_4)$.

Curing: Organic peroxides ; e.g., benzoyl peroxide, tertiary butylhydroperoxide, tertiary butylbenzoate, and cumene hydroperoxide will promote cure. Conventional paint driers will serve to introduce O from the air and can be used to polymerize LP-2. Cobalt driers are outstanding for this purpose.

Compatibility Data :

In the data given below solutions were prepared by stirring small increments of solvent into weighed quantities of the liquid polymer and continuing until precipitation or cloudiness occurred. The figures given indicate the ultimate tolerance of **LP-2** for the solvent. Thus **70%** for methylethyl ketone indicates 70% of the ketone and 30% LP-2 by weight. At **100%**, dilution is infinite.

Solvent	%	Solvent	%
glacial acetic acid	20	cyclohexanone	100
methanol	0	aniline	10
ethanol	0	benzene	100
diethyl ether	20	toluene	100
dioxane	100	carbon tetrachloride	70
petroleum ether	10	ethyl acetate	100
acetone	50	dibutylphthalate	100
methylethylketone	70	nitromethane	60

These figures do not hold for polymerized **LP-2** which has low solubility. Use in Pyrotechnics: As a fuel when polymerized.

Refs.

All data from Thiokol Corporation, Trenton, N.J., Ref. **59**

TITANIUM, Ti

Refs.

Specification No. :	MIL-T-13405A (CmlC)	
Molecular Weight :	47.90	
Crystalline Form (at temperatures up to about 800°C) :	α , hexagonal β , cubic	1
above transition :	silver grey to dark grey	1
Color :	(solid) 4.50	
Density, g./ml. :		
Coefficient of Thermal Expansion, linear (α) at R.T. :	8×10^{-6}	38
Temp. Range °C	Coefficient	
-195 to +20	6.8×10^{-6}	27
20-200	8.9×10^{-6}	
20-400	9.9×10^{-6}	
20-800	10.1×10^{-6}	
Heat of Formation, Kcal./mole at 298°K :	(gas) 112.6	5
Free Energy of Formation, Kcal./mole at 298°K :	(gas) 101.944	5
Entropy, cal./deg./mole at 298°K :	(c) 7.33	2, 5
	(gas) 43.07	1, 5
See Tables a and b		
Melting Point :	1940°K (1667°C)	4
Heat of Fusion, cal./mole :	3700	5
Boiling Point :	3550°K (2277°C)	5
Heat of Vaporization, cal./mole :	102,500	5
Transition Point, hexagonal (α) to cubic (β) :	1155°K (882°C)	4, 5, 9
Heat of Transition, cal./mole :	850	4
Heat of Sublimation, cal./mole at 298°K :	112,600	5
Heat Content or Enthalpy, cal./mole at 298°K :	(solid) 1150	5
	(gas) 1802	
See Tables a and b		

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	625	1.80	1500	9600	12.06
500	1250	3.20	1600	10,350	12.53
600	1920	4.42	1700	11,100	12.99
700	2610	5.48	1800	11,850	13.42
800	3330	6.44	1900	12,600	13.82
900	4070	7.31	1940 (β)	12,900	13.98
1000	4840	8.12	1940 (l)	17,360	16.28
1100	5638	8.87	2000	17,840	16.52
1155 (α)	6070	9.26	2200	19,440	17.29
1155 (β)	7020	10.09	2400	21,040	17.98
1200	7350	10.38	2600	22,640	18.62
1300	8100	10.98	2800	24,240	19.21
1400	8850	11.53	3000	25,840	19.77

Titanium, Ti (page 2)

Ti (α) :

Enthalpy : $H_T - H_{298.15} = 5.25T + 1.26 \times 10^{-3}T^2 - 1677$ (0.3percent ; 298–1155°K)

Heat Capacity : $C_p = 5.25 + 2.52 \times 10^{-3}T$

Ti (β) :

Enthalpy : $H_T - H_{298.15} = 7.50T - 1650$ (0.1 percent ; 1155–1940°K)

ΔH_{1940} (fusion) = 4450

Ti (l) :

Enthalpy : $H_T - H_{298.15} = 8.00T + 1840$ (0.1 percent ; 1940–3000°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	575	1.67	1900	8495	9.87
500	1120	2.88	2000	9075	10.16
600	1650	3.84	2200	10,275	10.74
700	2170	4.64	2400	11,530	11.28
800	2685	5.33	2600	12,840	11.79
900	3195	5.94	2800	14,210	12.31
1000	3705	6.47	3000	15,635	12.81
1100	4215	6.96	3500	19,460	13.98
1200	4730	7.40	4000	23,630	15.10
1300	5245	7.82	4500	28,110	16.15
1400	5765	8.20	5000	32,855	17.15
1500	6290	8.57	6000	42,895	18.98
1600	6825	8.91	7000	53,320	20.59
1700	7370	9.24	8000	63,830	21.99
1800	7930	9.56			

5, 9

38

Titanium, Ti (page 3)

X-Ray Crystallographic Data :					1
System	Space Group	a	c	Atoms/Unit Cell	
hexagonal	D _{6h}	2.951	4.692	2	
cubic		3.283		2	
Hygroscopicity (cumulative increase in weight after)					
Storage over H ₂ O for 29 days :			1.7%		51
H ₂ SO ₄ for 29 days :			0.0%		
Two days in oven at 105°C :			0.0%		
Solubility Data: In cold water:			insoluble		29
In hot water:			decomposes		
In dilute acids on heating:			soluble		
Health Hazard :			none ;physiologically inert		12
Safety Classifications:					
QSM :			class 2		
ICC : Powder listed under "Explosives and Other Dangerous Articles" as a flammable solid ;yellow label.					
U.N. :			inflammable solid		
Fire and Explosion Hazard : Powdered metal exposed to air is a dangerous fire hazard and burns with intense heat. Prevent water from contacting the material. Store and process in rooms or buildings adequately vented at the highest point to prevent the accumulation of hydrogen gas which results from the reaction of powdered metal and moisture. When mixed with oxidizing material, the powdered metal is a dangerous fire and explosion hazard. In the repair and maintenance of buildings or equipment, powder or dust should be removed and nonsparking tools used.					14, 49, 51
Finely ground titanium powder explodes spontaneously when in contact with hot air, and burns in atmospheres other than air. At 680°C, the fine powder burns in pure carbon dioxide. At red heat, titanium decomposes steam to free hydrogen. Above 1475°F it burns vigorously in atmosphere of pure nitrogen. The metal and its alloys explode when treated with nitric acid. Oil covered titanium chips have ignited spontaneously.					
Precautions When Handling Titanium :					
Titanium powder is shipped and stored wet. Moisture content of containers of titanium powder should be kept above 20% by volume. All standard precautions must be taken when handling the powder. Metal equipment with which it comes in contact must be grounded, and operations carried out in atmospheres of helium, or argon. Atmospheres of carbon dioxide and nitrogen are ineffective since dust layers of the powder ignite in these gases.					14
Electrostatic Sensitivity (minimum energy required for ignition of powder by electric sparks, millijoules) :					26
			(dust cloud) 10		
			(dust layer) .008		
Ignition Temperature, °C :					
Massive metal in air			700-800		12
Powder in air			250		12
Dust Cloud			330		26
Dust Layer			380		26

Titanium, Ti (page 4)

Minimum Explosive Concentration :

Powdered metal, mg./l.

45

26

Corrosion Resistance : Extremely resistant to corrosion by most substances.

38

Use in Pyrotechnics : As a fuel. According to the specification, it is used in first fire mixtures for incendiary munitions.

Additional References :

- 1) "The Explosive Characteristics of Titanium, Zirconium, Thorium, Uranium and Their Hydrides," I. Hartmann et al., Bureau of Mines R.I. 4835 (1951)
- 2) Ref. 64
- 3) L. G. Carpenter, Nature 263, 527 (1949)
- 4) J. Phys. Chem. 59, 127-131 (1955)

TITANYUM DIOXIDE, TiO_2 (Titania, Titanium White, Rutile, Anatase, Brookite)		Refs.
Percent Oxygen :	40.05	1, 29
Specification No. :	TT-T-425a (Dry-Paint F pigment)	
The specification covers one grade and three types of titanium dioxide pigment which vary in purity :		
Type I, Free chalking (anatase)		
II, Semi-chalking, aluminum treated (rutile)		
III, Chalk-resisting, silicon-aluminum-zinc-treated (rutile)		
Molecular Weight :	79.90	
Crystalline Form :	tetragonal	1
Allotropic Forms: TiO_2 occurs in four allotropic forms; brookite, rutile, and two forms of anatase. The stability fields of these modifications have not been clearly determined, but anatase II is reported to transform to anatase I at 642°C , and anatase I to rutile at 915°C . The first transformation is rapid; the second slow. The formation of a rutile structure also has been found to occur when Ti_2O_3 is oxidized.		65
Color: (purified titania) translucent water white or yellowish cast. Turns yellow then brown when heated.		29 54V7
Density, g./ml. :	(solid) brookite 4.17 octahedrite, anatase, 3.84 rutile 4.26	P 1, 22 1
Coefficient of Thermal Expansion :	9×10^{-6}	41
Ref. quotes Addnl. Ref. 5		
Coefficient of Thermal Expansion per $^\circ\text{C}$:	$(E \times 10^{-7})$ where E is 70-80 over the range 20-600 $^\circ\text{C}$	Addnl. Ref. 4
Heat of Formation, Kcal./mole at 298°K :	(c, 111) rutile, -218.0	1, 9
See Table a		
Free Energy of Formation, Kcal./mole at 298°K :	(c, 111) rutile, -203.8	
See Table a		
a. HEAT AND FREE ENERGY OF FORMATION OF TiO_2 (rutile)		2
T, $^\circ\text{K}$	ΔH (cal./mole)	ΔF° (cal./mole)
298.16. . . .	-225,500 (± 250)	-212,300 (± 250)
400	-225,350	-207,800
500	-225,100	-203,450
600	-224,900	-199,150
700	-224,700	-194,850
800	-224,500	-190,600
900	-224,300	-186,400
1000	-224,150	-182,200
1100	-224,000	-178,000
1150	-223,950	-175,900
1150	-224,900	-175,900

Titanium Dioxide, **TiO₂** (page 2)

$T, ^\circ K$	ΔH (cal./mole)	ΔF° (cal./mole)
1200	-224,800	-173,800
1300	-224,600	-169,550
1400	-224,400	-165,300
1500	-224,150	-161,100
1600	-223,900	-156,950
1700	-223,650	-152,750
1800	-223,400	-148,600
1900	-223,150	-144,450
2000	-222,850	-140,300

Free Energy Equations:		2
<i>Reaction</i>	<i>Range of Validity, °K</i>	
1) $Ti (\alpha) + O_2 (g) = TiO_2$ (rutile)	298.16-1150	
$\Delta F_T^\circ = -228,360 - 12.80T \log T + 1.62 (10^{-3}T^2) + 1.975 (10^5T^{-1}) + 82.81T$		
2) $Ti (\beta) + O_2 (g) = TiO_2$ (rutile)	1160-2000	
$\Delta F_T^\circ = -228,380 - 7.62T \log T + .36 (10^{-3}T^2) + 1.975 (10^5T^{-1}) + 68.431$		
Entropy, cal./deg./mole at 298°K :	(c, III) rutile, 12.01	9
See Tables b, c		
Melting Point:	2108°K (1835°C)	9
Heat of Fusion, Kcal./mole :	15.5 ± 2.5	24
Boiling Point :	(rutile) 2500°K (2227°C)	63
Heat of Vaporization, Kcal./mole :	138.9	Addnl. Ref. 1
Transition Point :	—	
Heat of Sublimation :	—	
		4

$T, ^\circ K$	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg.	$T, ^\circ K$	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	1540	4.43	1300	17,000	24.38
500	3100	7.91	1400	18,820	25.73
600	4735	10.89	1500	20,660	27.00
700	6440	13.51	1600	22,530	28.20
800	8160	15.81	1700	24,420	29.35
900	9900	17.86	1800	26,340	30.44
1000	11,650	19.70	1900	28,280	31.49
1100	13,420	21.39	2000	30,250	32.50
1200	15,200	22.94			

Enthalpy : $H_T - H_{298.15} = 17.97T + 0.14 \times 10^{-3}T^2 + 4.35 \times 10^5T^{-1} - 6829$
 (0.8 percent ; 298-1800°K)

Heat Capacity : $C_p = 17.97 + 0.28 \times 10^{-3}T - 4.35 \times 10^5T^{-2}$

Titanium Dioxide, TiO₂ (page 3)

c. HEAT CONTENT AND ENTROPY OF TiO₂(anatase)
(Base, crystals at 298.15°K)

4

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	1540	4.43	900	9930	17.89
500	3100	7.91	1000	11,720	19.78
600	4735	10.89	1100	13,530	21.51
700	6440	13.52	1200	15,350	23.09
800	8170	15.82	1300	17,180	24.55

TiO₂ (anatase) :

Enthalpy : $H_T - H_{298.15} = 17.83T + 0.25 \times 10^{-3}T^2 + 4.23 \times 10^{-5}T^3 - 6767$
(0.7percent ; 298-1300°K)

Heat Capacity : $C_p = 17.83 + 0.50 \times 10^{-3}T - 4.23 \times 10^{-5}T^2$

Heat Capacity, cal./deg./mole: (solid) 13.16

See equations above

Decomposition Temperature: —

Decomposition Products: —

Dissociation Pressures: —

Vapor Pressure, $\log p_{\text{atm.}} = -\frac{30361}{T} - 0.492 \times 10^{-3} + 11.19$ (T=OK)

at 2000°K, $\log p = 4.97$ atm. See also Ref. 54V6

9

63

Addnl. Ref. 1

X-Ray Crystallographic Data :

1

System	Space Group	a	c	Molecules/ Unit Cell
(rutile) tetragonal	D _{4h} ¹⁴	4.58	2.95	2

Hygroscopicity : nonhygroscopic

Solubility Data : In water, HCl, HNO₃, dil. H₂SO₄ : insoluble

1

In hot concentrated H₂SO₄, alkalies : soluble

Health Hazard : Considered harmless but high concentrations of the dust may cause irritation to the respiratory tract.

12, 25

M.A.C., mg./m.³ of air : (tentative) 15

29

Safety Classifications :

OSM : not listed

ICC : not listed

Fire and Explosion Hazard: none

Electrostatic Sensitivity : —

Use in Pyrotechnics : a product of the combustion of Ti

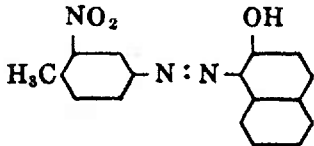
Additional References :

- 1) "Vapor-Solid Equilibria in the Titanium Oxygen System," W. Groves et al., J. Phys. Chem. 59, 127 (1955)
- 2) Ref. 64
- 3) For color changes see also Ref. 44V29 sup
- 4) F. Hummel and E. Henry, Report 6, Penn. State College School of Mineral Industries, PB 60, 659 (1946) ; cited by Ref, 65
- 5) Ind. Eng. Chem. 38, 1097 (1946)

TOLUIDINE-RED TONER (dry paint pigment)
(1-(3-Nitro-p-Tolueneazo)-2-Naphthol,
Metanitroparatoluidino-azo-Betanaphthol, C.I. 12120,
C.I. Pigment Red 3)

Refs.

82, 48A

Formula :		$C_{17}H_{13}N_3O_3$	
Specification No.:	TT-T-562		
The color shall be resistant to HNO_3 (1.20 Sp. Gr.), to HCL (1.10 Sp. Gr.) and to 10% caustic soda solution.			
Molecular Weight :	307.32		
Crystalline Form :	microscopic delicate feathery needles	82	
Color :	purplish or brown ; bright red to somewhat darker yellowish red	82 Spec. 84A	
Density, g./ml. :	(solid) 1.40 (bulking value) 0.08576	82 82	
Coefficient of Thermal Expansion :	—		
Heat of Formation:	—		
Free Energy of Formation:	—		
Entropy:	—		
Melting Point, °C:	258	48A	
Heat of Fusion:	—		
Boiling Point:	—		
Transition Point :	—		
Heat of Sublimation :	—		
Heat Content or Enthalpy :	—		
Heat Capacity :	—		
Decomposition Temperature :	—		
Decomposition Products :	—		
Vapor Pressure :	—		
X-Ray Crystallographic Data :	—		
Hygroscopicity:	—		
Solubility Data : In acetone and chloroform :	soluble	82	
In alcohol and benzene :	slightly soluble	48A	
In hot water :	very slightly soluble	82	
Health Hazard :	—		
Safety Classifications :	—		

Toluidine-red toner (page 2)

Fire and Explosion Hazard:

Electrostatic Sensitivity :

Resistance to light :

(full shade) excellent

82

(tint) good

to heat:

to 320°F

poor when baked 20 min.

at 270°F

to acids and alkalies:

good

Use in Pyrotechnics: Added to igniter compositions to impart a red color for identification.

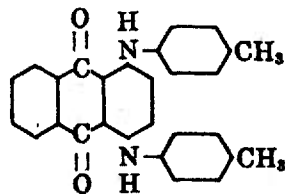
Additional References :

- 1) Ref. 82

1,4-di-p-TOLUIDINOANTHRAQUINONE
(1,4-di-p-tolyaminoanthraquinone,
D & C Green No. 6, Quinizarine
Green G Base, C.I. 61565, C.I. Solvent Green 3)

Refs.
92, 48A

Formula :



C₂₈H₂₂N₂O₂

Specification No. :

MIL-D-3277

Molecular Weight:

418.5

Crystalline **Form** :

needles

88V14

Color : Green, from chlorobenzol — blue,
 from glacial acetic acid - dark violet

88V14

88V14

Density, g./ml.

Apparent Density :

(Spec.) **0.45 ± 0.25**

Temperature Coefficient :

—

Heat of Formation:

—

Free Energy of Formation :

—

Entropy:

—

Melting Point:

491°K (218°C)

88V14

Heat of Fusion:

—

Boiling Point:

—

Transition Point :

—

Heat of Sublimation :

—

Heat Content or Enthalpy :

—

Heat Capacity :

—

Decomposition Temperature :

—

Decomposition Products :

—

Vapor Pressure :

—

X-Ray Crystallographic Data :

—

Hygroscopicity :

—

Solubility Data : In alcohol (g./l.) at 60°C :

34

Addnl. Ref. 1

In aniline:

soluble with green color

88V14

In concentrated H₂SO₄ :

soluble with violet-blue
 color or violet-red

In chloroform and in benzene :

soluble

Health Hazard :

unknown

92

1,4-Di-p-toluidinoanthraquinone (page 2)

Safety Classification:

OSM :

not listed

ICC :

not listed

Fire and Explosion Hazard:

—

Electrostatic Sensitivity :

—

Use in Pyrotechnics:

to color smoke mixtures
green

, Additional References:

- 1) "The Dyeing Phenomena of Acetate Artificial Silk," V. Kartaschoff and G. Farine, *Helv. Chim. Acta* 2,822 (1928)

TUNGSTEN, W (Wolfram)

Refs.

Specification No. :	MIL-T-13827	
Molecular Weight :	183.86	
Crystalline Form :	(cubic) p-form trans- forms irreversely to α above 700°C	5
Color :	grey-black	
Density, g./ml. :	(solid) 19.3	
Coefficient of Thermal Expansion, linear :		
-108 to 0°C :	4.2×10^{-6}	1
0-100 :	4.3×10^{-6}	
0-300 :	4.5×10^{-6}	
0-500 :	4.6×10^{-6}	
1000-2000 :	6.1×10^{-6}	
Heat of Formation, cal./mole at 298°K :	(gas) -200,000	5
Free Energy of Formation, cal./mole at 298°K :	(gas) -190,009	1, 5
Entropy, cal./deg./mole at 298°K :	(gas) 41.55	5
	(c) 8.04	
See Tables b, c		
Melting Point, °K :	3650	5
Heat of Fusion, cal./mole :	8420	5, 7
Boiling Point:	5800°K (5427°C)	5
Heat of Vaporization, cal./mole :	191,000	5
Transition Point:	—	
Heat of Sublimation, cal./mole :	200,000	5
Heat Content or Enthalpy, cal./mole :	(solid) 1216	5
	(gas) 1486	
Heat Capacity :	(solid) 5.92	5
	(liquid) 8.5	
	(gas) 7.5	

T, °K	C _p ° cal./deg./mole	T, °K	C _p ° cal./deg./mole
298	5.92	1600	7.00
600	6.17	2000	7.33
800	6.34	2500	7.74
1000	6.50	3000	8.15
1200	6.67		

See also equations below

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	mole
400	615	1.77	1500	7730	10.18
500	1220	3.12	1600	8430	10.63
600	1830	4.23	1700	9130	11.06
700	2450	5.19	1800	9840	11.47
800	3080	6.03	1900	10,550	11.85
900	3710	6.77	2000	11,270	12.22
1000	4360	7.46	2200	12,720	12.91
1100	5010	8.08	2400	14,190	13.55
1200	5670	8.65	2600	14,680	14.14
1300	6340	9.19	2800	17,190	14.70
1400	7030	9.70	3000	18,720	15.23

W(c) :

Enthalpy : $H_T - H_{298.15} = 5.74T + 0.38 \times 10^{-3}T^2 - 1745$ (0.4 percent ; 298-3000°K)Heat Capacity : $C_p = 5.44 + 0.76 \times 10^{-3}T$

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	540	1.55	1500	10,150	12.47
500	1130	2.86	1600	11,048	13.04
600	1805	4.09	1700	11,895	13.56
700	2580	5.28	1800	12,730	14.04
800	3440	6.44	1900	13,540	14.47
900	4375	7.53	2000	14,325	15.61
1000	5354)	8.56	2200	15,855	14.88
1100	6340	9.50	2400	17,330	16.25
1200	7325	10.36	2600	18,780	16.83
1300	8200	11.14	2800	20,210	17.36
1400	9235	11.84	3000	21,635	17.85

W(g) :

Enthalpy : $H_T - H_{298.15} = 10.70T - 0.66 \times 10^{-3}T^2 + 4.64 \times 10^5T^{-1} - 4688$
(0.3 percent ; 1600-3000°K)Heat Capacity : $C_p = 10.70 - 1.32 \times 10^{-3}T - 4.64 \times 10^5T^2$

Tungsten, W (page 3)

Vapor Pressure: At 2000–3500°K can be calculated from $\log p(\text{mm. Hg.}) = -\frac{4200}{T} + 9.84 - 0.0146 \log T - 0.164T$. Where T = temperature °K. Vapor pressure is 1 mm. at 3990°C

X-Ray Crystallographic Data :

<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>Atoms/Unit Cell</i>
α , cubic	O_h^3	3.1583	2
β , cubic	O^2 or O_h^3	5.04	8

Hygroscopicity :

Solubility Data : In water :

In HNO_3 , H_2SO_4 , and aqua regia :

In HF and HNO_3 :

Health Hazard :

Safety Classifications :

OSM :

insoluble

very slightly soluble

soluble

very slight

class 2

Fire and Explosion Hazard : Tungsten is dangerous in the powdered form when exposed to flame. It burns with intense heat. Prevent water from contacting the material. Store and process only in **room** or buildings adequately vented at the highest point to prevent the accumulation of hydrogen gas which results from the reaction of the powdered metal and moisture.

When compounded with oxidizing agents, the powdered metal is a dangerous fire and explosion hazard. In the repair or maintenance of buildings or equipment, powder or dust should be removed and nonsparking tools used.

Electrostatic Sensitivity :

Use in Pyrotechnics:

as a fuel

Additional References :

- 1). "Tungsten," C. J. Smithells, Chapman & Hall Ltd., London (1952)
- 2) Ref. 46

TUNGSTEN DIOXIDE, WO ₃		Refs.
Specification No. :	—	
Molecular Weight :	215.92	1A
Crystalline Form :	cubic	1A
Color :	brown	1A
Density, g./ml. :	(solid) 12.11	1A
Coefficient of Thermal Expansion :	—	
Heat of Formation, Kcal./mole at 298°K :	(c) -134.0 ± 2.5 -136.3	24A 1A, 9, 31A
Free Energy of Formation, Kcal./mole at 298°K :	(c) -123.8 -122 -118	6 8 31A
HEAT AND FREE ENERGY OF FORMATION OF WO ₃ (c)		2

Entropy, cal./deg./mole at 298°K :	15 15.5 16.0 ± 2.5	6 2 24A
Melting Point, °K : See Decomposition Temperature below. Ignites in air. Ignites in nitrogen at 1500–1600°C.		3PA
Heat of Fusion, Kcal./mole :	11.5	6
Boiling Point : Begins to sublime at about 800°C. Quite volatile above 1050°. The boiling point is about 1800°K.		44S54
Heat of Vaporization, Kcal./mole :	48.86	44354
Heat of Sublimation :	—	
Heat Content or Enthalpy :	—	
Heat Capacity :	—	
Decomposition Temperature, °K :	decomposes at 2125 ± 50	8
Decomposition Products :	W + WO ₃ which sublimes	44S54

Tungsten Dioxide, WO_2 (page 2)

Vapor Pressure :

appreciable at 1800°K

44S54

X-Ray Crystallographic Data :

System	Space Group	a	b	c	Axial Angle	Molecules/ Unit Cell	
monoclinic	P_{21}	5.65	4.89	5.56	$120^\circ 25'$	4	4, 24A
tetragonal	D_{4h}^{14}	4.86		2.77		2	2, 1A, 97

Hygroscopicity :

—

Solubility Data : In H_2O , acids, KOH :

insoluble

1A

Health Hazard:

slightly toxic

Safety Classifications :

OSM :

not listed

ICC :

not listed

Fire and Explosion Hazard : The amorphous powder is strongly pyrophoric and easily oxidized to WO_3 .

50V14

Electrostatic Sensitivity :

—

Use in Pyrotechnics :

—

ZINC, Zn

Refs.

Specification No. :	JAN-Z-365	
Covers three grades, which differ in purity, and two classes differing in granulation.		
Molecular Weight :	66.38	1
Crystalline Form :	hexagonal	1
Color :	bluish-white	1
Density, g./ml. :	(solid) 7.14	1
Coefficient of Thermal Expansion, linear at		
10-100°C :	26.28×10^{-6}	1
cubic at 0-100°C :	89.28×10^{-6}	
Equation for linear coefficient: $l_t = l_0 (1 + .2969 \times 10^{-4} t - .0635 \times 10^{-7} t^2)$		1
where l_t = length at temp. t in °C and l_0 = length at 0°C		
Heat of Formation, Kcal./mole at 298°K :	(gas) 31.18	1, 9
Free Energy of Formation, Kcal./mole at 298°K :	(gas) 22.682	5
Entropy, cal./deg./mole, at 298°K :	(c) 9.95 (gas) 38.45	1, 5 1, 5
See Tables a and b		
Melting Point :	692.7°K (419.6°C)	4, 5
Heat of Fusion, cal./mole :	1765	1, 5
Boiling Point :	1181°K (908°C)	5
Heat of Vaporization, cal./mole :	27,960	5
Transition Point :	—	
Heat of Sublimation, cal./mole	31,180	5
Heat Content or Enthalpy, cal./mole :	(solid) 1349	5
See equations below		

4

°K	cal./mole	cal./deg. mole		cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	625	1.80	800	5150	9.08
500	1270	3.24	900	5900	9.96
600	1940	4.46	1000	6650	10.75
692.7 (c) . . .	2580	5.45	1100	7400	11.47
692.7 (f) . . .	4345	8.00	1200	8150	12.12
700	4400	8.08			

b. HEAT CONTENT AND ENTROPY OF Zn (g)
(Base, ideal gas at 298.15°K)

4

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	505	1.46	1900	7960	9.20
500	1005	2.57	2000	8455	9.46
600	1500	3.48	2200	9450	9.93
700	1995	4.24	2400	10,445	10.36
800	2495	4.90	2600	11,440	10.76
900	2990	5.49	2800	12,435	11.13
1000	3490	6.01	3000	13,425	11.47
1100	3985	6.49	3500	15,910	12.24
1200	4480	6.92	4000	18,400	12.90
1300	4980	7.32	4500	20,905	13.49
1400	5475	7.69	5000	23,435	14.03
1500	5975	8.03	6000	28,675	14.98
1600	6470	8.35	7000	34,385	15.86
1700	6965	8.65	8000	40,905	16.73
1800	7465	8.94			

Zn (g) :Enthalpy: H_T - H_{298.15} = 4.971' - 1482(0.1 percent ;298-5000°K)

Heat Capacity, cal./deg./mole :

(solid) 6.07
(liquid) 7.50
(gas) 4.97

4, 5

Also see above

Decomposition Temperature :

Decomposition Products :

Vapor Pressure :

Press. mm.	1	10	40	100	400	760	M.P.	1
Temp. °C	487	593	673	736	844	907	419.4	

X-Ray Crystallographic Data :

System	Space Group	a	c	Atoms/Unit Cell
hexagonal	D _{6h} ⁴	2.6585	4.9342	2

Hygroscopicity : On exposure to moist air zinc becomes coated with a white basic carbonate of Zn. Cumulative increase in weight after :

16, 29

Storage over H₂O for 29 days :

5.2%

51

Storage over H₂SO₄ for 29 days :

4.7%

Two days in oven at 105°C :

4.3%

Solubility Data : Insoluble in water, but soluble in acids, alkalies, and ammonia.

1, 29

Zinc, Zn (page 3)

Health Hazard : Zinc powder is slightly to moderately toxic. When heated fumes of ZnO evolve, which when inhaled can cause "brass founders ague" or "brass chills" and fever, also called "zinc-fume fever," "zinc chills" or "galvo." The effect is usually temporary.	93, 12, 25, 29
M.A.C. of zinc (asZnO) ,mg./m. ³ :	15
Safety Classifications :	14
OSM :	class 2
ICC :	not listed
Fire and Explosion Hazard : Powdered zinc when heated is an explosive and fire hazard. It burns with intense heat. Prevent water from contacting the material. Store and process only in buildings or rooms adequately vented at the highest point to prevent the accumulation of evolved hydrogen gas . When compounded with oxidizing agents, the powdered metal is a dangerous fire and explosive hazard. In the repair or maintenance of buildings or equipment, powdered dust should be removed and nonsparking tools used. Fight fire with special mixtures of dry chemicals, or powdered talc .	12, 14, 49, 51
See also Ref. 86	75
Electrostatic Sensitivity (minimum energy required for ignition of powder by electric sparks,millijoules) :	(dust cloud) 650
Ignition Temperature, °C :	(dust cloud) 20'
	(dust layer) 100
Minimum Explosive Concentration, mg./l. :	480
Use in Pyrotechnics: As a fuel. On burning, it produces a white light with a bluish-green or bluish tint.	20, 29

ZINC CARBONATE

Refs.

Formula :	ZnCO ₃				
Specification No.:	MIL-Z-12061				
Molecular Weight :	125.39				
Crystalline Form :	trigonal	1			
Color:	white	29			
	colorless	1			
Density, g./ml. :	(solid) 4.44	1			
Coefficient of Thermal Expansion :	_____				
Heat of Formation, Kcal./mole at 298°K :	(c) -194.2	9			
Free Energy of Formation, Kcal./mole at 298°K :	(c) -174.8	9			
Entropy, cal./deg./mole at 298°K :	19.7	3, 9			
Melting Point :	loses CO ₂ at 573°K (300°C)	1			
Heat of Fusion :	_____				
Boiling Point :	_____				
Transition Point :	_____				
Heat of Sublimation:	_____				
Heat Content or Enthalpy:	_____				
Heat Capacity, cal./deg./mole :	(solid) 19.16	9			
Molal Heat Capacity can be estimated from $C_p = 9.30 + 33.0 (10^{-3}T)$ at 298-780°K		4			
Decomposition Temperature :	loses CO ₂ at 300°C				
Commercial ZnCO ₃ gives off some CO ₂ even at 90°C. Decomposition is complete at 300° in 1 hour, and at 400° in 1/2 hour.		1			
Decomposition Products :	ZnO + CO ₂	54V4			
Heat of Dissociation, cal./mole :	21,000	54V2			
Dissociation Pressure :	A constant reproducible decomposition pressure has not been observed. The decomposition depends on the grain size and other factors.	44332 sup			
X-Ray Crystallographic Data :					
<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>Axial Angle</i>	<i>Molecules/ Unit Cell</i>	
hexagonal	D _{3d} ⁶	5.704	$\alpha = 48^\circ 6'$	2	1
Hygroscopicity :			_____		
Solubility Data :					
In water at 15°C :				0.001 g.	1, 12
In acids, alkalies, NH ₄ salts :				soluble	
In NH ₃ , acetic acid, pyridine :				insoluble	
Health Hazard :			low		

Zinc Carbonate (page 2)

Safety Classifications:

OSM :

ICC :

Fire and Explosion Hazard:

Electrostatic Sensitivity :

Use in Pyrotechnics :

not listed

not listed

as a retardant

17

ZINC OXIDE, ZnO
(Chinese White, Zinc White, Flowers of Zinc,
Zinc Bloom, Philosopher's Wool)

Refs.
1, 11, 29

Specification No.:	MIL-Z-291B	
The specification covers three grades of which grades 1 and 2 are used in pyrotechnic mixtures. They differ somewhat in purity (grade 2 is the purer) and have the same granulation.		
Molecular Weight:	81.88	
Crystalline Form:	amorphous powder	1
Color:	white (or yellowish)	1
	Becomes lemon yellow on heating, regaining its white color on cooling.	52V11
Density, g./ml.:	(solid) 5.47	1
Coefficient of Thermal Expansion, cubical:	(aver.) 1.8×10^{-7}	31
Heat of Formation, Kcal./mole at 298°K:	(fused) -84.36 (c) -83.17	1, 9
See Table a		
Free Energy of Formation, Kcal./mole at 298°K:	(c) -76.06	1, 9
See Table a		
a. HEAT AND FREE ENERGY OF FORMATION OF ZnO (c)		2

T, °K	A H (cal./mole)	A F° (cal./mole)
298.16. . . .	-83,250 (± 200)	-76,100 (± 200)
400	-83,150	-73,650
500	-83,050	-71,300
600	-82,950	-68,950
692.7	-82,850	46,800
692.7	-84,600 •	-66,800
700	-84,600	-66,600
800	-84,560	-64,050
900	-84,500	-61,460
1000	-84,400	-58,900
1100	-84,300	66,860
1180	-84,200	-54,350
1180	-111,600	-54,350
1200	-111,560	-53,350
1300	-111,150	-48,500
1400	-110,750	-43,700
1500	-110,350	-38,950
1600	-109,900	-34,200
1700	-109,460	-29,600
1800	-109,000	-24,800
1900	-108,560	-20,160
2000	-108,100	-15,500

Zinc Oxide, ZnO (page 2)

Phase Changes of Metal
M.P., 692.7°K ; $\Delta H = 1765 \text{ cal./g.-atom}$
B.P., 1180°K ; $\Delta H = 27,430 \text{ cal./g.-atom}$

Free Energy Equations :

<i>Reactions</i>	<i>Range of Validity, °K</i>
1) $\text{Zn (c)} + \frac{1}{2} \text{O}_2 \text{ (g)} = \text{ZnO (c)}$ $\Delta F_T^\circ = -84,670 - 6.40 (T \log T) + .84 (10^{-3} T^2) + .99 (10^5 T^{-1}) + 43.25 T$	298.16–692.7
2) $\text{Zn (l)} + \frac{1}{2} \text{O}_2 \text{ (g)} = \text{ZnO (c)}$ $\Delta F_T^\circ = -85,520 - 1.45 (T \log T) - .36 (10^{-3} T^2) + .99 (10^5 T^{-1}) + 31.25 T$	692.7–1180
3) $\text{Zn (g)} + \frac{1}{2} \text{O}_2 \text{ (g)} = \text{ZnO (c)}$ $\Delta F_T^\circ = -115,940 - 7.28 (T \log T) - .36 (10^{-3} T^2) + .99 (10^5 T^{-1}) + 74.94 T$	1180–2000

Entropy, cal./deg./mole at 298°K :

See Tables b, c

Melting Point :

> 2073°K (> 1800°C)
zincite, 2243°K (1975°C)
4470

Heat of Fusion, g./cal./mole :

decomposes

Boiling Point :

zincite, decomposes
2223°K (1950°C)

Transition Point :

Sublimation Temperature :

2073°K (1800°C)

Heat of Sublimation, Kcal./mole :

111–112.5

$T, ^\circ\text{K}$	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	$T, ^\circ\text{K}$	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	1070	3.08	1300	12,120	17.29
500	2190	5.58	1400	13,450	18.28
600	3350	7.69	1500	14,800	19.21
700	4530	9.51	1600	16,160	20.09
800	5740	11.13	1700	17,530	20.92
900	6970	12.57	1800	18,910	21.71
1000	8220	13.89	1900	20,300	22.46
1100	9500	15.11	2000	21,700	23.18
1200	10,800	16.24			

ZnO (c) :

Enthalpy : $H_T - H_{298.15} = 11.71 T + 0.61 \times 10^{-3} T^2 + 2.18 \times 10^5 T^{-1} - 4277$
(0.4 percent ;298–2000°K)

Heat Capacity : $C_p = 11.71 + 1.22 \times 10^{-3} T - 2.18 \times 10^5 T^{-2}$

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	795	2.28	1000	5875	9.99
500	1605	4.10	1200	7630	11.59
600	2435	5.61	1400	9390	12.95
700	3285	6.92	1600	11,160	14.13
800	4140	8.06	1800	12,930	15.17
900	5005	9.08	2000	14,710	16.11

ZnO (g) : Enthalpy : $H_T - H_{298.15} = 8.40T + 0.17 \times 10^{-3}T^2 + 0.82 \times 10^5T^{-1} - 2795$ (0.3 percent ; 298-2000°K) Heat Capacity: $C_p = 8.40 + 0.34 \times 10^{-3}T^2 - 0.82 \times 10^5T^{-2}$ Heat Capacity, cal./deg./mole at 298°K: (solid) 9.62											9
Temp, °K	20	30	50	100	450	200	300	500	700	900	44S32 sup
C _p	0.17	0.60	1.98	4.24	6.22	7.20	9.66	11.2	11.8	12.3	
Also see equations above											
Decomposition Temperature, °K :							2250 ± 25		8		
Heat of Decomposition [to Zn(g) and O(g)]											
Kcal./mole :							< 92		44S32 sup		
Decomposition Products :to Zn +O (1673-1748°K)									Addnl. Ref. 3		
Vapor Pressure:											
Approx. Press. mm.			0.1	1.2	3.5	12	760	Addnl. Ref. 1			
Temp. °C			1000	1400	1450	1500	1700				
For Dissociation Pressure vs. Temp. see Ref. 54V4 and 44V32 sup											
X-Ray Crystallographic Data :											
System	Space Group		a	c	Molecules/ Unit Cell			1			
hexagonal	C _{6v} ⁴		3.24265	5.1948	2						
Hygroscopicity: Absorbs H ₂ O and CO, from air. The rate of absorption is greater the finer the oxide and increases with rising temp.											44S32 sup
Solubility Data: In water:							.00016 g./100 ml. at 29°C				
In mineral acids, dilute acetic acid, NH ₄ OH :							soluble		1		
Health Hazard: Slight to moderately toxic. Zinc oxide is relatively inert, and virtually harmless except when freshly formed. It is an eye irritant, however, and should not be allowed to come into contact with the eyes. Fresh fumes of zinc oxide can cause "brassfounders ague" or "brass chills," etc.											93
(See Zinc.)											25
M.A.C. mg./m. ³ of air for an 8hr. working day : 15											29
											14

Zinc Oxide, ZnO (page 4)

Safety Classifications :

OSM : not listed
ICC: not listed

Fire and Explosion Hazard: none listed

Precautions When Handling:

Handle carefully to avoid excessive "dusting." Keep work area clean, and wash hands frequently.

Store in sealed containers away from acids.

If it enters the eye, thorough washing of the eye in a bubble type fountain or inverted faucet will remove the irritating particles. Take the victim to a physician immediately for examination and further treatment.

Electrostatic Sensitivity : _____

Use in Pyrotechnics: A product of the burning or oxidation of zinc. Used in screening smoke compositions.

Additional References :

- 1) "Zinc Oxide Rediscovered," H. E. Brown, New Jersey Zinc Company, New York
- 2) Ref.64
- 3) "The Stability of Gaseous Diatomic Oxides," Brewer and Mastic, J. Chem. Phys., 19,834 (1951)

ZINC STEARATE

Refs.

Formula: $\text{Zn}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$
 Specification No.: _____
 Molecular Weight: 632.30
 Crystalline Form: Light powder, talc-like to touch, usually marketed as a fine powder about 300-325 mesh.
 Color: white
 Density: _____
 Coefficient of Thermal Expansion: _____
 Heat of Formation: _____
 Free Energy of Formation: _____
 Entropy: _____

16, Addnl. Ref. 1

Melting Point: 403°K (130°C)
 Melts to a clear water-white liquid and cools to a translucent glassy mass of crystalline appearance and which is easily powdered.

1 Addnl. Ref. 1

Heat of Fusion: _____
 Boiling Point: _____
 Transition Point: _____
 Heat of Sublimation: _____
 Heat Content or Enthalpy: _____
 Heat Capacity: _____
 Decomposition Temperature: _____
 Decomposition Products: _____
 Vapor Pressure: _____
 X-Ray Crystallographic Data: _____

Hygroscopicity: nonhygroscopic (repels water)

29

Solubility Data:

In water, alcohol, ether: insoluble
 In benzene: soluble

1

Temp. °C	CH ₃ OH	Toluol
25	0.04*	0.04*
50	0.06	0.27
75	1.88	1.98
100	6.56	4.97

Addnl. Ref. 2

*g. of stearate/100 g. solvent.

For additional solubility data see Addnl. Ref. 3

Health Hazard: low
 Inhalation of the powder can lead to pulmonary inflammation.

2, 29

Safety Classifications:

OSM: not listed
 ICC: not listed

Zinc Stearate (page 2)

Fire and Explosion Hazard:

Autoignition Temp., °F :	790	12, 71

Flash Point (open cup), °F :	530	

Electrostatic Sensitivity :

Use in Pyrotechnics :	as a retardant, fuel, and binder	17

Additional References :

- 1) "Metallic Soaps—Their Uses, Preparation and Properties," W. F. Whitmore and M. Lauro, Ind. Eng. Chem., 42, 646 (1930)
- 2) "Aero Metallic Stearates," (pamphlet) American Cyanamid Co. (1960)
- 3) "The Solubility of Zinc Soaps in Organic Solvents," E. P. Martin and R. C. Pink, J. Chem. Soc. 1750 (1948)

ZIRCONIUM, Zr

Refs.

Specification No.:	PAPD-464	
Specification PAPD-464 covers two classes which differ in purity. A type of zirconium powder has been developed which is made by a new process, and has three granulations A, B, and C . This new type is covered by new specification FA-PD-MI-2364. Granulations A and B of this type are packed , shipped, and handled dry. Granulation C of this type is packed , shipped, and stored under water.		
Molecular Weight :	91.22	
Crystalline Form :	cubic	1
Color: The bulk metal is silvery white to grey. Dry colloidal Zr and finely pulverized Zr are black and resemble carbon in appearance. Coarser granulations are steel-grey in color and look like crushed cast iron.		1, 28, 29
Density, g./ml. :	(solid) 6.49	39
Coefficient of Thermal Expansion, linear :		28, 39, 50V15
hexagonal, α form (298–1143°K)—linear		
along a axis :	6.5×10^{-6}	
along c axis:	10.8×10^{-6}	
cubic, β (1143–1600°K) :	9.7×10^{-6}	
Range °C	Coeff. (linear)	27
–183 to 0	$4.0\text{--}5.1 \times 10^{-6}$	
0–20	$4.6\text{--}5.9 \times 10^{-6}$	
20–200	5.4×10^{-6}	
20–400	6.1×10^{-6}	
20–700	7.1×10^{-6}	
Heat of Formation, Kcal./mole at 298°K:	(gas) 125	1
Free Energy of Formation, Kcal./mole at 298°K :	(gas) 115	9
Entropy, cal./deg./gm. at 298°K :	(c) 9.29 (gas) 43.31	5
See Tables a and b		
Melting Point:	2125°K (1832°C)	5
Heat of Fusion, cal./mole:	4000	5
Boiling Point :	4650°K (4377°C)	5
Ref. 39 gives 3577°C (3850°K). Other refs. vary appreciably.		
~~Heat~~ of Vaporization, cal./mole:	139,000	5
Transition Point, °K :	1135	5, Addnl. Ref. 2
Heat of Transition, cal./mole :	920	2
Heat of Sublimation, cal./mole :	146,000	5
Heat Content or Enthalpy, cal./mole at 298°K:	(solid) 1313	5
See equations below		

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	650	1.87	1600	10,680	12.98
500	1330	3.39	1700	11,470	13.46
600	2030	4.66	1800	12,260	13.91
700	2730	5.76	1900	13,050	14.33
800	3460	6.72	2000	13,840	14.74
900	4200	7.59	2100	14,630	15.12
1000	4980	8.41	2130 (c) . . .	14,870	15.24
1100	5800	9.20	2130 (l) . . .	19,770	17.54
1135 (α) . . .	6090	9.46	2200	20,330	17.80
1135 (β) . . .	7005	10.26	2400	21,930	18.49
1200	7520	10.70	2600	23,530	19.13
1300	8310	11.33	2800	25,130	19.72
1400	9100	11.92	3000	26,730	20.28
1500	9890	12.47			

Zr (α) :

Enthalpy: $H_T - H_{298.15} = 6.50T + 0.71 \times 10^{-5}T^2 + 0.82 \times 10^5T^{-1} - 2276$
(0.7 percent; 298–1135°K)

Heat Capacity: $C_p = 6.50 + 1.42 \times 10^{-5}T - 0.82 \times 10^5T^{-2}$

Zr (β) :

Enthalpy: $H_T - H_{298.15} = 7.90T - 1960$ (0.1 percent; 1135–2130°K)
 ΔH_{2130} (fusion) = 4900

Zr (l) :

Enthalpy: $H_T - H_{298.15} = 8.00T + 2730$ (0.1 percent; 2130–3000°K)

b. HEAT CONTENT AND ENTROPY OF Zr (g)
(Base, ideal gas at 298.15°K)

T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole	T, °K	H _T - H _{298.15} cal./mole	S _T - S _{298.15} cal./deg. mole
400	665	1.92	1900	10,325	11.92
500	1325	3.39	2000	11,025	12.28
600	1980	4.58	2200	12,450	12.96
700	2620	5.57	2400	13,905	13.59
800	3245	6.40	2600	15,390	14.18
900	3870	7.13	2800	16,900	14.74
1000	4475	7.78	3000	18,435	15.27
1100	5085	8.36	3500	22,410	16.50
1200	5705	8.90	4000	26,575	17.61
1300	6335	9.40	4500	30,925	18.63
1400	6970	9.87	5000	35,430	19.58
1500	7620	10.32	6000	44,750	21.28
1600	8280	10.75	7000	54,235	22.74
1700	8950	11.15	8000	63,645	24.00
1800	9630	11.54			

Zirconium, Zr (page 3)

Zr (g) :

Enthalpy : $H_T - H_{298.15} = 7.01T - 0.35 \times 10^{-3}T^2 + 0.38 \times 10^5T^{-1} - 2186$
(0.7percent ; 298-1400°K)

Heat Capacity : $C_p = 7.01 - 0.70 \times 10^{-3}T - 0.38 \times 10^5T^{-2}$

Enthalpy : $H_T - H_{298.15} = 5.59T + 0.36 \times 10^{-3}T^2 - 0.50 \times 10^5T^{-1} - 1631$
(0.3percent ; 1400-6000°K)

Heat Capacity : $C_p = 6.69 + 0.72 \times 10^{-3}T + 0.50 \times 10^5T^{-2}$

Heat Capacity, cal./deg./mole **at 298°K :** (liquid) 8.00
(α form) 6.01
(β form) 7.90

c. HEAT CAPACITY OF Zr

(Solid I, 298-1143°K ; Solid II, 1143-2125°K ;
Liquid, 2125-3000°K)

$T, ^\circ K$	C_p° (cal./deg./mole)
298	6.01
400	6.36
600	6.88
800	7.34
1000	7.79
1100	8.01
1200	6.79
1600	7.43
2000	8.07
2100	8.23
2200	
to	
3000	8.00

See also equations above

Decomposition Temperature : _____

Decomposition Products : _____

Vapor Pressure : For 1949-2054°K the following equation holds :

$\log P$ (atm.) = $-31,066/T + 7.3351 - 2415 \times 10^{-4}$ (where T = absolute temp.)

Press. atm.	10^{-4}	10^{-3}	10^{-2}	1
Temp. °K	2450	2700	3000	3850

X-Ray Crystallographic Data :

System	Space Group	a	c	Molecules/Unit Cell
hexagonal	D_{6h}^4	3.223	5.123	2
cubic	O_h^2	3.61		

Hygroscopicity : _____

Solubility Data: Insoluble in water. Soluble in HF, aqua regia, hot phosphoric acid. Slightly soluble in acids.

Zirconium, Zr (page 4)

Safety Classifications:

OSM : (dust) class 1
 ICC : flammable solid ;
 yellow label

Fire and Explosion Hazard: Dry Zr powder or sponge is a pyrophoric solid liable to spontaneous combustion and burns in air with intense heat. It may explode particularly in the presence of water due to evolution of hydrogen. The explosive range of dust clouds of Zr powder in air is about 45 to 300 mg./l. The range of fire and explosion is **increased** by heat and the presence of oxidizers. **12, 14, 15, 26, 28**

Caution: **Do** not use water to fight fire. Use special mixtures of dry chemical salt, dry sand, or powdered talc. Use only nonsparking tools for repair or maintenance in storage areas. **49, 51, 75**

Health Hazard: Zirconium powder is believed to be nontoxic. Zirconium and its alloys explode when treated with nitric acid. **93**

M.A.C. mg./m.³ : 5 **12**

Precautions When Handling :

Zirconium powder (PAPD) is shipped and stored wet. In no case should it be shipped and stored in anything larger than a one-gallon can, nor should the moisture content be reduced to less than **25** percent by volume. Powder containing 5-15% water is extremely dangerous. When once ignited, it burns even more violently than the dry powder. All operations with the powdered metal must be performed in an inert atmosphere, and persons working with it require protective clothing including gloves and face protection. Waste zirconium powder, rags, and other materials that have come in contact with it must be segregated from other wastes, immersed in water, and disposed of at once. At ordinary temperature Zr is not very reactive as a thin protective coating of oxide on the surface is formed. **28**

Zr readily combines with oxygen and the rate is appreciable at 200°C. The energy of activation of the reaction has been determined as 18.2 Kcal./mole and the entropy of activation as -25.6 cal./mole.

Zr combines not only with oxygen, but also with nitrogen, carbon, and silicon. **16**

At high temperatures Zr burns with a brilliant white light. When the hot metal is treated with steam at 700-800°C, free hydrogen is evolved. **39**

Autoignition Temperature : 500°F **75**

See FA-PD-M 1-2364 for handling the new type of Zr.

Electrostatic Sensitivity (minimum energy required for ignition of powder by electric sparks, millijoules) : **26**

(dust cloud) 5
 (dust layer) 0.001

Use in Pyrotechnics: As a fuel, and a component of nongaseous fuze powders. **17**

Additional References :

- 1) "The Explosive Characteristics of Titanium, Zirconium, Thorium, Uranium, and Their Hydrides," I. Hartmann et al., Bureau of Mines, RI4835 (Dec. 1951)
- 2) "Metallurgy of Zirconium," B. Lustman and F. Kerze, Jr., McGraw-Hill Book Company, New York (1955) for data on the various physical properties of Zr.

ZIRCONIUM HYDRIDE, ZrH_2 (not a definite chemical)

Refs.

Zirconium readily absorbs hydrogen even at room temperature, forming brittle, metallic-like materials whose compositions vary with the amount of hydrogen absorbed and approach ZrH_2 as the limiting maximum hydrogen content. The absorption is reversible and at constant pressure decreases with increasing temperature. The optimum temperature for absorption of H by Zr is given as $300^\circ C$. However, the data of Addnl. Ref. 4 show a higher absorption at 20° and $150^\circ C$, i.e., **24,000 cc. at S.T.P. per 100 g. of metal and 23,700 cc. at $300^\circ C$** . The absorption of H by Zr is exothermic and results in a large increase in volume, approximately 15%. The absorbed H_2 is completely liberated at about $800^\circ C$. Absorption depends to some extent on the surface condition of the Zr.

28, 39, Addnl.
Ref.1 i

Zirconium hydrides have been prepared by

- 1) Heating the prepared metal with H_2 .
- 2) Forming the metal in the presence of H_2 .
- 3) Treating ZrO_2 with CaH_2 at $600-1000^\circ$ in an atmosphere of H_2 .

Although Zr and H_2 do not form definite compounds, five well-defined crystal phases of the two are recognized. These have been designated α , β , etc. The ϵ phase is a face-centered tetragonal phase which includes the range from $ZrH_{1.67}$ to close to ZrH_2 , and corresponds to about 66.7 atom % of H_2 .

Specification No. :	MIL-Z-21353	
Molecular Weight :	93.24	
Crystalline Form :	powder	1
Color :	dark grey to black	1, 29
Density, g./ml. :	(solid) 5.6 5.74	12 50V15
Coefficient of Thermal Expansion :	—	
Heat of Formation for $ZrH_{1.99}$, Kcal./mole :	38.9	50V15
Free Energy of Formation :	—	
Entropy :	—	
Melting Point :	—	
Heat of Fusion :	—	
Boiling Point :	—	
Transition Point :	—	
Heat of Sublimation :	—	
Heat Content or Enthalpy :	—	
Heat Capacity :	—	
Decomposition Temperature :	apparent above $100^\circ C$	28
Decomposition Products :	hydrogen driven off	
Vapor Pressure :	—	

Zirconium Hydride, ZrH₂ (page 2)

X-Ray Crystallographic Data (for a hydrogen content approaching ZrH₂) :

System	Space Group	a	c	Molecules/ Unit Cell	
tetragonal		4.364	4.440		28
tetragonal (ε phase)		3.513	4.450	4	Addnl. Ref. 3 44542
Hygroscopicity :		—			
Solubility Data :		—			
Health Hazard :		—			
Safety Classifications :		—			
OSM :			not listed		
ICC :			not listed		
Fire and Explosion Hazard :	Dangerous, due to evolution of hydrogen. At higher temperatures ZrH ₂ reacts with oxygen and with oxygen containing compounds. It may ignite and explode with water.				12, 39
See also Ref. 44V42					
Electrostatic Sensitivity (minimum energy required for ignition of powder by electric sparks, millijoules) :			(dust cloud) 60 (dust layer) .064		26
Activation Energy, at 1 atm., cal./mole :			17,200± 200		17
Use in Pyrotechnics:			in igniting flares and as a fuel		
Minimum Explosive Concentration of Zirconium Hydride Powder, mg./l. :					26
See Also Addnl. Ref. 1			85		
Autoignition Temperature, 300–600°C :			(dust cloud) 350 (dust layer) 270		28, 26
Additional References :					
1) T. B. Douglas and A. C. Victor, J. Research N.B.S. 61, 13 (1958)					
2) “The Explosive Characteristics of Titanium, Zirconium, Thorium, Uranium and Their Hydrides,” I. Hartmann et al., Bureau of Mines, RI 4835 (1951)					
3) “The Crystal Structures of ThH ₂ and ZrH ₂ ”, R. Rundle et al., Z. Phys. Chem. 11B, 433 (1931)					
4) Hall et al., Tran. Far. Soc. 41, 306 (1945) cited in Ref. 40					

ZIRCONIUM-NICKEL ALLOY (Powdered)

Refs.

Formula:	(Spec.) Zr/Ni: 70/30 and 30/70
Specification No.:	MIL-Z-11-110A
The specification covers two types. Type I is a 70/30 and Type II a 30/70 Zr/Ni alloy.	
Molecular Weight:	-----
Crystalline Form:	cubic
Color:	silver white to grey
Density, g./ml.:	(solid) 6.4
Coefficient of Thermal Expansion:	-----
Heat of Formation:	-----
Free Energy of Formation:	-----
Entropy:	-----
Melting Point:	-----
Heat of Fusion:	-----
Boiling Point:	-----
Transition Point:	-----
Heat of Sublimation:	-----
Heat Content or Enthalpy:	-----
Heat Capacity:	-----
Decomposition Temperature:	-----
Decomposition Products:	-----
Vapor Pressure:	-----
X-Ray Crystallographic Data:	-----
Hygroscopicity:	-----
Solubility Data:	resistant to acids and alkalies
Health Hazard:	-----
Safety Classifications:	
OSM:	(dust) class 2
ICC:	not listed
Fire and Explosion Hazard: The specification requires that the alloy be packed in heat sealed inert plastic liners, such as polyethylene, in new clean metal containers.	
Electrostatic Sensitivity:	-----
Use in Pyrotechnics:	as a fuel; a vigorous deoxidizer

Additional References:

- 1) For the Zr-Ni system up to 40% Ni see E. T. Hayes et al., "The Zirconium-nickel diagram," Trans. Amer. Soc. Metals, 45 893 (1953)