SUPPORTING INFORMATION

Heat of Decomposition Estimates

	$3\ N_2H_{4\ (l)}$	⟶	$N_{2\ (g)}$	+	$4\ NH_{3\ (g)}$
$\Delta H_{f,}$ (kJ/mole) =	50.63		0.00		-46.11
ΔH_{rxn} (kJ/mole) =	-112.11				

Figure 1. Heat of decomposition estimate using heats of formation for liquid hydrazine decomposing to nitrogen and ammonia (heats of formation from NBS Tables[1]).

	$3\ N_2H_{4\ (g)}$	⟶	$N_{2\ (g)}$	+	$4\ NH_{3\ (g)}$
$\Delta H_{f,}$ (kJ/mole) =	95.40		0.00		-46.11
ΔH_{rxn} (kJ/mole) =	-156.88				

Figure 2. Heat of decomposition estimate using heats of formation for gaseous hydrazine decomposing to nitrogen and ammonia (heats of formation from NBS Tables[1]).

Some of the important properties of hydrazine and hydrazine hydrate are summarized in the tables below.

Table 1. Hydrazine properties[2]

Identity	
CAS	302-01-2
Formula	H_2NNH_2
Physical Properties	
Appearance	colorless, fuming, hygroscopic liquid.[3]
Melting point	2.0 °C [4]
Boiling point	113.5 °C[4]
Heat of formation, 298 °K, liquid	+50.434 kJ/mole
Heat of fusion	12.657 kJ/mole
Heat of vaporization, at normal boiling point	39.079 kJ/mole
Density	1.004 g/ml at 25 °C[4]
Vapor pressure	0.014 atm at 20 °C[5]
pH (1% solution)	10.1-10.7[4]
Miscible solvents	Water and alcohol
Immiscible solvents	Chloroform, Ether
Flammability Properties	
Closed cup flash point	38 °C[4,6,7]
Flammability range (LFL measured at 100 °C)	4.7-100% at 100 °C[4,8,9, 10]
Autoignition temperature	178 °C[11]

Lower pressure limit at room temperature[12]	0.014 atm[13]
Heat of combustion (upper) for Hydrazine liquid[14]	-622 kJ/mole[6]
Vapor detonable?	Yes
Liquid detonable?	No
Other	May self-heat to ignition if spilled onto porous or fibrous materials
Thermal Stability	
Heat of decomposition for liquid	-112 kJ/mole (3500 J/g) assuming decomposition to N_2 and NH_3.[15]
Exotherm detection temperature	Generally > 200 ^{o}C, but can be much lower if exposed to certain metals, metal oxides, or organic materials.
Toxicity	
Toxicity	Toxic by ingestion, inhalation, and skin absorption; strong irritant to skin and eyes; a carcinogen (US OSHA)3; readily absorbed through the skin.
Carcinogenicity Level	IARC 2B (confirmed animal carcinogen – possibly human carcinogen)[16]
NIOSH Immediately Dangerous to Life and Health (IDLH) concentration	50 ppm[17]
US OSHA Permissible Exposure Limit (PEL)	1 ppm TWA
ACGIH Threshold Limit Value (TLV)	0.01 ppm TWA[18]
NIOSH Recommended Exposure Limit (REL)	0.03 ppm[19]
Lethal Dose - 50% probability (LD50) Oral -	60 mg/kg[10]

rat	
Lethal Dose - 50% probability (LD50) Dermal - rabbit	91 mg/kg[10]
Lethal Concentration - 50% probability (LC50) Inhalation - mouse - 4 hr	252 ppm[10]
Toxicity to fish; LC50 - Poecilia reticulata (guppy)	0.28 mg/l - 96.0 h (very toxic)[10]
Odor threshold	3-5 ppm[20]

Transportation	
UN Number	2029
UN and US CFR[21] Classification	8 (Corrosives); subsidiary classifications 3 (Flammable Liquid) and 6.1 (Toxic Substance); packing group I

Table 2. Hydrazine hydrate properties (see Table 1 for toxicity and miscibility information)[22]

Identity	
CAS	7803-57-8
Formula	$H_2NNH_2 \cdot H_2O$
Physical Properties	
Appearance	colorless, fuming liquid
Wt% hydrazine	64
Melting point	-51.7 ^oC
Boiling point	119.4 ^oC
Vapor pressure	0.0097 atm at 20 ^oC[23]
Partial pressure hydrazine	0.0039 atm (3900 ppm) at 20 ^oC[23]
Density	1.032 g/ml

Vapor-liquid equilibrium data	Exhibits an azeotrope; see Figure 3 for data at 1 atmosphere.
Flammability	
Flash Point	73 °C (open cup)
Fire Point	74 °C[24]
Transportation	
UN Number	2030
UN and US CFR description[21]	HYDRAZINE AQUEOUS SOLUTION, with more than 37% hydrazine, by mass
UN and US CFR Classification[21]	8 (Corrosives); subsidiary classification 6.1 (Toxic Substance); packing group I, II, or III[25]

Table 3. 25 wt% Aqueous hydrazine properties (see Table 1 for toxicity and miscibility information).

Physical Properties	
Appearance	Colorless liquid
Wt% hydrazine	25
Melting Point	-30 °C[26]
Boiling Point	107 °C[23]
Vapor Pressure	0.025 atm at 25 °C[23]
Partial Pressure hydrazine	0.00086 atm (860 ppm) at 25 °C[23]
Vapor-liquid equilibrium data	Distills to an azeotrope; see Figure 3 for data at 1 atmosphere.
Flammability	
Flash Point	No flash point
Transportation	

UN Number	3293
UN and US CFR classification[21]	6.1 (Toxic Substance); packing group III
UN and US CFR description[21]	HYDRAZINE AQUEOUS SOLUTION, with not more than 37% hydrazine, by mass

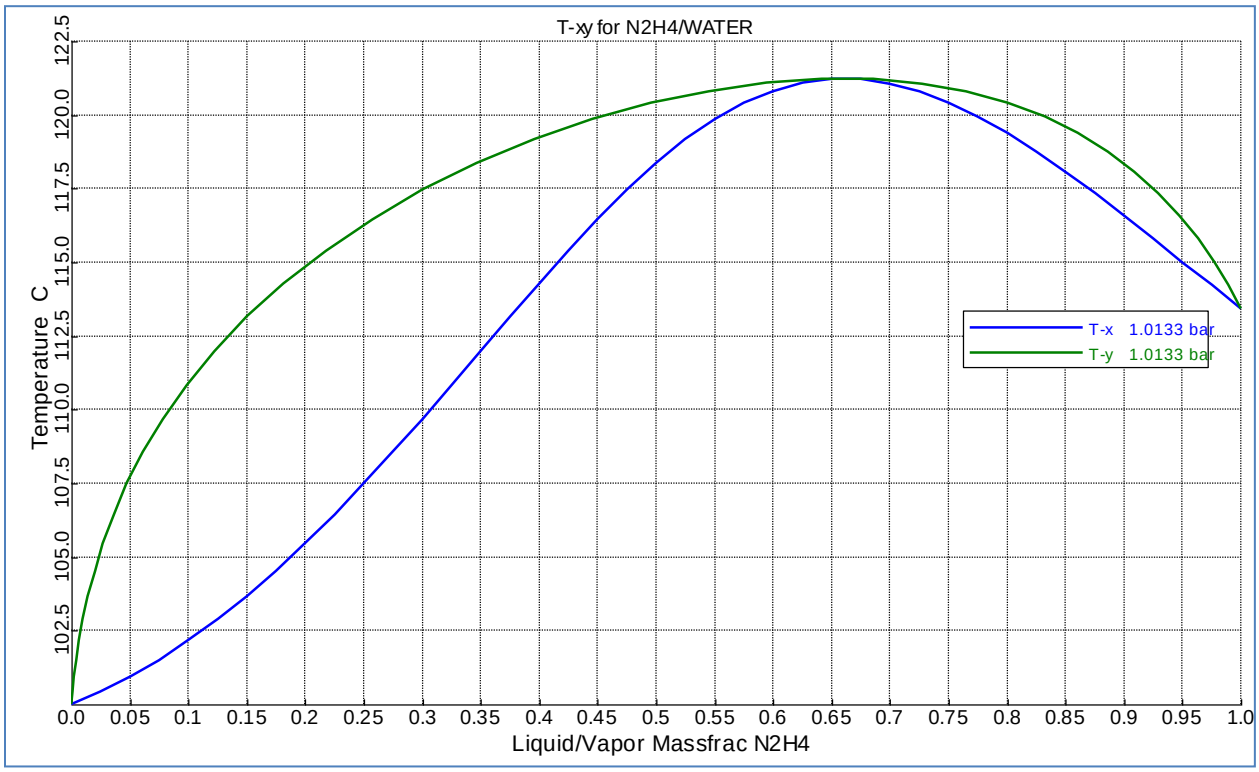

Figure 3. Txy plot for hydrazine-water mixtures at 1 atmosphere (from Aspen® software using default NRTL Binary Interaction Parameters).

ABBREVIATIONS

ACGIH	American Conference of Governmental Industrial Hygienists
TLV	Threshold Limit Value
LFL	Lower Flammability Limit
ARC	Accelerating Rate Calorimeter
LC50	Median Lethal Concentration of substance in air
LOAEL	Lowest-Observed-Adverse-Effect level
NIOSH	National Institute for Occupational Safety and Health
IDLH	Immediately Dangerous to Life and Health
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Level
PAC-2	Protective Action Criteria level 2; an estimate of the concentration which for a 60 minute exposure may hinder the ability to escape or may cause irreversible or other serious health effects
EPA	US Environmental Protection Agency
NBS	US National Bureau of Standards
IARC	International Agency for Research on Cancer
TWA	Time Weighted Average
LD50	Median Lethal Dose
UN	United Nations
CFR	US Code of Federal Regulations
NRTL	Non-Random Two Liquid model
SARA	Superfund Amendments and Reauthorization Act of 1986
CAA	Clean Air Act
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
EPCRA	Emergency Planning and Community Right-to-Know Act

RMP	Risk Management Plan
AIAA	American Institute of Aeronautics and Astronautics
CFR	Code of Federal Regulations

REFERENCES

[1] The NBS Tables of Chemical Thermodynamic Properties, American Chemical Society and the American Institute of Physics for the National Bureau of Standards, Wagman D. D., et al., 1982.

[2] In addition to the references listed, most of this information can also be found in Schmidt (ref 2 in the article) along with extensive discussion.

[3] "Hawley's Condensed Chemical Dictionary", 15th ed., John Wiley and Sons, 2007.

[4] Arch Chemicals information (http://www.archchemicals.com/Fed/HDR/Products/Propellants/Ultra.htm).

[5] Literature vapor pressure data for anhydrous hydrazine is conveniently summarized in Aspen Properties®.

[6] "Ignition Handbook", Babrauskus, Fire Science Publishers, 2003.

[7] Explosive decomposition of hydrazine by rapid compression of a gas volume, Bunker, R. L.; Baker, D. L.; Lee, J. H. S., Progress in Astronautics and Aeronautics, (1991), 133, 325-41.

[8] F. E. Scott, J. J. Burns, and B. Lewis, Explosive Properties of Hydrazine, Report of Investigations 4460, U.S. Dept. of the Interior, Bureau of Mines, Pittsburgh, Pa., May 1949.

[9] Based on an analysis of closed cup flash point data it appears the LFL is actually 4.0%. See the Flammability section.

[10] Aldrich MSDS.

[11] Highly variable. Hydrazine may partially decompose at test temperatures thereby changing the concentration tested. In addition, autoignition temperature varies with the equipment set due to variable heat losses and the potential for catalytic effects.

[12] The lower pressure limit is the total pressure below which it was not possible to obtain ignition under test conditions.

[13] Fire, Explosion, Compatibility, and Safety Hazards of Hypergols – Hydrazine, AIAA Special Project SP-084-1999, American Institute of Aeronautics and Astronautics, 1999.

[14] Upper heating value (assumes liquid water is a product rather than water vapor).

[15] See Thermal Stability section.

[16] IARC (International Agency for Research on Cancer) Monographs (http://monographs.iarc.fr/ENG/Classification/index.php).

[17] NIOSH (US National Institute for Occupational Safety and Health; http://www.cdc.gov/niosh/idlh/302012.html).

[18] Aldrich MSDS quoted ACGIH (American Conference of Governmental Industrial Hygienists) value.

[19] As published in the US National Institute for Occupational Safety and Health (NIOSH) Pocket Guide (http://www.cdc.gov/niosh).

[20] Arch Chemicals information (http://www.archchemicals.com/Fed/HDR/Products/Hydrates/responsiblecare.htm).

[21] See the UN Recommendations on the Transport of Dangerous Goods, and the US Code of Federal Regulations (49 CFR 172.101) for more information.

[22] Much of this information can also be found at the Arch Chemicals website (see ref 57 in the article) and in Schmidt (ref 2 in the article).

[23] Calculations performed using Aspen Plus® (Aspen Technology Inc.) software.

[24] Arch Chemicals information (http://www.archchemicals.com/Fed/HDR/Products/Hydrates/default.htm).

[25] UN 2030 can have a packing group of I, II, or III, depending on its corrosivity and toxicity, which are functions of concentration. See the UN Recommendations on the Transport of Dangerous Goods, and the US Code of Federal Regulations (49 CFR 172.101) for more information.

[26] "Kirk-Othmer Encyclopedia of Chemical Technology", John Wiley and Sons, 1999.