

**Lecture 5: Chemical Thrusters for In-Space Propulsion**

**HYDRAZINE**

Hydrazine was first isolated by Curtius in 1887, and in 1907 a suitable synthetic method was developed by Raschig. Anhydrous hydrazine is a clear, colorless, hygroscopic liquid with an odor similar to that of ammonia. Anhydrous hydrazine is a strong reducing agent and a weak chemical base. Aqueous hydrazine shows both oxidizing and reducing properties. Although potential data show hydrazine to be a powerful oxidizing agent in acidic solutions, reactions with many reducing agents are so slow that only the most powerful ones reduce it quantitatively to ammonium ion. Hydrazine will react with carbon dioxide and oxygen in air. When hydrazine is exposed on a large surface to air, such as on rags, it may ignite spontaneously due to the evolution of heat caused by oxidation with atmospheric oxygen. A film of hydrazine in contact with metallic oxides and other oxidizing agents may ignite.

Hydrazine is an endothermic compound and will decompose spontaneously in a similar way to hydrogen peroxide. The reaction of hydrazine with the oxides of copper, manganese, iron, silver, mercury, molybdenum, lead or chromium may be particularly violent. The spontaneous or artificially induced decomposition of hydrazine does not follow the reaction  $N_2H_4 = N_2 + 2H_2$ , but a more exothermic one such as  $2N_2H_4 = 2NH_3 + N_2 + H_2$ .

**SUMMARY AND CONTENTS**

<u>PHYSICO-CHEMICAL PROPERTIES</u>	<u>METRIC</u>	<u>VALUE</u>	<u>ENGLISH</u>	<u>REFERENCE</u>	<u>FIGURE</u>
Molecular Formula		$N_2H_4$		(1)	
Molecular Weight		32.04		(1)	
Freezing Point	1.5°C		34.7°F	(6)	
Freezing Point Diagram with Additives					1
Boiling Point	113.5°C		236.3°F	(10)	4
Critical Properties		$P_c = 145 \text{ atm.}$ $T_c = 380^\circ\text{C} (716^\circ\text{F})$ $d_c = 0.231 \text{ g/cc}$		(5) (5) (5)	3 3 3
Density, liquid	1.0045 g/cc @ 25°C		8.482 lb/gal @ 77°F		2, 3
Density, vapor and liquid				(5)	3
Vapor Pressure	14.38 mm @ 25°C		0.0189 atm @ 77°F	(6)	4
Surface Tension	66.67 dynes/cm @ 25°C 62.32 dynes/cm @ 35°C		.004568 lb/ft @ 77°F .004270 lb/ft @ 95°F	(7) (9)	
Viscosity, liquid	0.90 centipoise @ 25°C		.000605 lb/ft -sec @ 77°F	(11, 12)	5
Heat Flux at $q_{ul}$ / Pressure				(8)	6
Heat Flux at $q_{ul}$ / Temperature				(8)	7
Heat Flux at $q_{ul}$ / Velocity				(8)	8

Heat of Fusion	3.025 kcal/mole @ 1.5°C		37.51 Btu/lb @ 34.7	(6)	
Heat of Vaporization	9.600 kcal/mole @ 113.5°C		54.0 Btu/lb @ 236°F	(3)	
Heat Capacity (liquid) Temp.	23.62 cal/mole-°C @ 25°C		.737 Btu/lb-°F @ 77°F	(6)	9
Heat of Combustion N <sub>2</sub> H <sub>4</sub> (l)+O <sub>2</sub> =N <sub>2</sub> +2H <sub>2</sub> O (l)	148.6 kcal/mole @ 25°C		8.346 Btu/lb @ 77°F	(20)	
Heats of Formation at 25°C (77°F) N <sub>2</sub> +2H <sub>2</sub> = N <sub>2</sub> H <sub>4</sub> (g) N <sub>2</sub> +2H <sub>2</sub> = N <sub>2</sub> H <sub>4</sub> (liq) N <sub>2</sub> +2H <sub>2</sub> +H <sub>2</sub> O = N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O N <sub>2</sub> +2H <sub>2</sub> + aq = N <sub>2</sub> H <sub>4</sub> . aq	22.750 kcal/mole 11.999 kcal/mole 10.300 kcal/mole 8.140 kcal/mole		1278 Btu/lb 675 Btu/lb 579 Btu/lb 457 Btu/lb	(20) (20) (20) (20)	
Index of Refraction, D		1.4644 @ 25°C (77°F)		(9)	
Dielectric Constant		51.7 @ 25°C (77°F)		(19)	
Electrical Conductivity		3 × 10 <sup>-6</sup> ohm <sup>-1</sup> @ 25°C (77°F)		(11)	
Flash Point (open cup)	52°C		126°F	(18)	
Explosive Limits (in air, 1 atm.)		4.7% lower 100% upper		(18) (18)	

B. Materials: The following table gives an evaluation of the compatibility data that are available for numerous metals, plastics, elastomers, and miscellaneous material:

**COMPARATIVE COMPATIBILITY OF VARIOUS MATERIALS WITH HYDRAZINE AND HYDRAZINE MIXTURES (Ref. 28)**

A-Material is acceptable for general service.  
B-Material is acceptable for limited service.  
C-Material which must be avoided.

MATERIAL	ANHYDROUS HYDRAZINE	HYDRAZINE HYDRATE	HYDRAZINE-HYDRAZINE NITRATE-WATER MIXTURES
<b>Metals</b>			
Aluminum			
2S	A	A	B
2SO	A	A	B
2SH	A	A	B
3S	A	A	B
3SH	A	A	B
24ST	A	A	A
40E	B	B	B
43	B	B	B
52ST	A	A	A

61ST	A	A	A
75ST	A	A	A
MATERIAL	ANHYDROUS HYDRAZINE	HYDRAZINE HYDRATE	HYDRAZINE- HYDRAZINE NITRATE- WATER MIXTURES
XA-545	B	B	B
716	B	B	B
Brass	B	B	B
Cobalt	C	C	C
Copper	C	C	C
Inconel	B	B	B
Inconel X	B	B	B
Iron	C	C	C
Lead	C	C	C
Magnesium	C	C	C
Manganese	C	C	C
Molybdenum	C	C	C
Monel	B	B	C
Nickel	B	B	C
Nickel-chrome alloys (Chromel-A, Nichrome)	B	B	C
Silver	B	B	B
Steel			
Mild	C	C	C
Stainless			
302	B	B	B
303	C	C	C
304	A	A	A
315	C	C	C
316	C	C	C
317	C	C	C
321	B	B	B
329	C	C	C
347	A	A	A
410	B	B	B
416	C	C	C
420F	C	C	C
430	B	B	B
430F	C	C	C
440A	C	C	C
440C	C	C	C
W	B	B	B
Stellite	B	B	B
Tantalum	A	A	A
Tin	C	C	C
Titanium	A	A	A
Zinc	C	C	C
<b>Plastics and Elastomers</b>			

Cellulose acetate	C	C	C
Diallyl phthalate	C	C	C
MATERIAL	ANHYDROUS HYDRAZINE	HYDRAZINE HYDRATE	HYDRAZINE- HYDRAZINE NITRATE- WATER MIXTURES
Epon	B	B	B
Ethyl cellulose	B	B	B
Furane resin	B	B	B
Hycar	B	B	B
Kel-F	B	B	B
Lactopreme	C	C	C
Lucite	B	B	B
Melamine formaldehyde	B	B	B
Nylon	B	B	B
Phenolic	B	B	B
Polyester	C	C	C
Polyethylene	A	A	A
Polystyrene and polydichlorostyrene	C	C	B
Polyvinyl alcohol	C	C	C
Polyvinyl chloride (Koroseal, Vinylite, etc.)	B	B	B
Rubber			
Natural gum	C	C	C
Synthetic	B	B	B
Saran	C	C	C
Silastic	B	B	B
Teflon	A	A	A
Tygon	B	B	B
U.S. Rubber			
Plastic			
L7825	B	B	B
M20995	B	B	B
Veloform	C	C	C
<b>Miscellaneous Materials</b>			
Asbestos	B	B	B
Glass			
Soft	A	A	A
Pyrex	A	A	A
Graphite	B	B	B
Graphitar	B		
Pipe-joint compounds			
AN-C-53	B	B	B
Oxyseal	B	B	B
Thread-Tite	B	B	B
Rags	C	C	C

Silicone lubricants			
DC-200 series	B	B	B
MATERIAL	ANHYDROUS HYDRAZINE	HYDRAZINE HYDRATE	HYDRAZINE- HYDRAZINE NITRATE- WATER MIXTURES
DC-550	B	B	B
DC-710	B	B	B
Plug-cock grease	B	B	B
Solder			
Lead-tin	B	B	B
Silver	B	B	B
Varnish	B	B	B
Wood	C	C	C
Wool	C	C	C

- C. Equipment: The selection of materials of construction of equipment for use with hydrazine should be limited to those previously listed as acceptable for general service.

#### Hydrazine and hydrazine rockets -

##### (1) Properties.

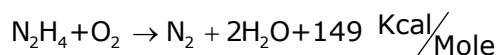
Hydrazine monopropellant rockets have become standard for NSSK and other on-board maneuvering needs. This is because of the simplicity of a monopropellant rocket, storability of hydrazine over many years, and relatively good performance achievable. Also, the technology of hydrazine engines is well developed. There had been other monopropellants used or considered before ( $H_2O_2$ , nitromethane) but they are inferior either in safety or in performance.

Formula:  $N_2H_4$

Clear, very similar to water in physical properties

( $\rho = 1 \text{ g/cm}^3$ , freezes at  $1.5^\circ\text{C}$ , boils at  $113.5^\circ\text{C}$ , surface tension =  $66.7 \text{ dyn/cm}$  at  $25^\circ\text{C}$ , viscosity =  $0.9 \text{ cp}$  at  $25^\circ\text{C}$ , specific heat  $0.72 \text{ cal/g}^\circ\text{C}$  at  $25^\circ\text{C}$ ). Other properties listed in the given table.

Chemically, however,  $N_2H_4$  is very different from  $H_2O$ . It will react with  $CO_2$  and  $O_2$  in air; if exposed to a large surface of air, as in wet rags, it may ignite; it may also ignite in contact with metallic oxides. Its combustion is very exothermic:



and so hydrazine is a good fuel for a bipropellant rocket (Hydrazine +  $O_2$ ). Variations are the monomethyl hydrazine (MMH)  $NH_2CH_3$  and the unsymmetric dimethyl hydrazine (UDMH,  $NH_2(CH_3)_2$ ), which are very similar but somewhat

inferior thermochemically, but have a wider liquid range. A popular bipropellant combination is A50 (50% hydrazine, 50% UDMH). These cannot be used as monoprops, because they poison the catalyst.

Hydrazine evolves  $\text{NH}_3$ , and smells like it. Its vapors damage the eyes and the pulmonary tract. The liquid, if pure, is fairly inert, but vapors form flammable mixtures in air for vapor pressures corresponding to  $T > 40^\circ\text{C}$ . The liquid decomposes exothermically if catalyzed by iron oxide, copper oxide, or oxides of Pb, Mn, Mb, Ag, Hg or Cr. It is not sensitive to friction or impact.

Materials compatibility is an important consideration, especially for long term storage and for parts of thrusters with long life exposed to it. Materials which are OK are aluminum, stainless 304 or 347, titanium, tantalum, rhenium and platinum. Also glass, Teflon and polyethylene plastics. To be avoided are copper, cobalt, iron, lead, magnesium, manganese, molibdenum, mild steel, high Mo stainless (416, 303), most plastics (except as noted), wood, rags, paper. See table handed out.

Oils are OK for lubrication, but not if there is a catalytic bed, since it gets poisoned by the oil. Hydrazine is expensive (\$ 50-60/lb for MMH, as of 1994).

## (2) Thermochemistry.

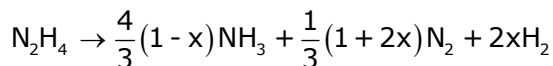
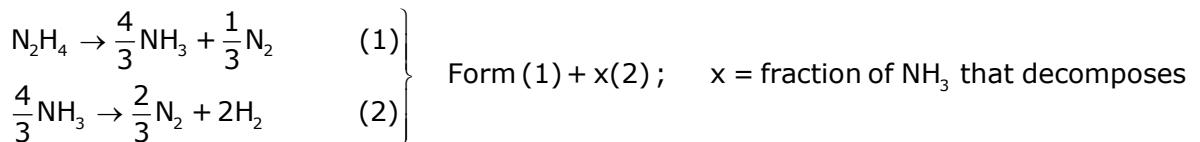
When catalyzed either by an oxide or by a hot platinum surface,  $\text{N}_2\text{H}_4$  decomposes. Since at low temperatures ammonia,  $\text{NH}_3$ , is stable, the preferred end products would be  $\text{NH}_3 + \text{N}_2$ :



However, this is a very exothermic reaction, and the equilibration T would be  $1650^\circ\text{K}$ , at which temperature  $\text{NH}_3$  is not stable anymore. Hence, the final equilibrium composition would contain very little  $\text{NH}_3$ , due to



and would be at intermediate T, since the latter reaction is endothermic. In practice reaction (a) is very fast (less than 1 msec) if catalyzed, while (b) is slow. Hence, for small decomposition chambers and high flow rates, when the residence time  $\rho_{\text{gas}} V_{\text{ch}} / \dot{m}$  is short, reaction (b) proceeds only partially, the extent being controllable by the design conditions. The final composition and overall reaction assuming a fraction x of  $\text{NH}_3$  decomposes is



For an adiabatic combustion (no heat loss, no heating), we must have (starting from liquid  $N_2H_4$  at  $298^\circ K$ )

$$h_{N_2H_4}(\ell, 298^\circ) = \frac{4}{3}(1-x)h_{NH_3}(T) + \frac{1}{3}(1+2x)h_{N_2}(T) + 2xh_{H_2}(T) \rightarrow \text{Equation for } T$$

The respective molar enthalpies can be fitted by

$$h_{NH_3}(T) = -16.83 + 12.35\theta + 0.983\theta^2 \frac{K_{cal}}{mole} \left( \theta = \frac{T}{1000^\circ K} \right)$$

$$h_{N_2}(T) = -2.83 + 7.75\theta + 0.183\theta^2$$

$$h_{H_2}(T) = -1.967 + 6.6\theta + 0.367\theta^2 \quad (300 \leq T \leq 4000^\circ K)$$

(Notice  $c_p$  (cal/mole $^\circ C$ )) is  $\frac{dh}{d\theta}$ , with h in Kcal/mole)

From the table given,  $h_{N_2H_4}(\ell, 298^\circ K) = 12$  Kcal/mole. We can now solve for T at various arbitrary values of x:

$$\theta = \frac{\sqrt{139.3 - 20.75x + 8.45x^2} - (9.525 + 0.95x)}{1.372 - 0.455x}$$

x (fraction of $NH_3$ decomposed)	0	0.2	0.4	0.6	0.8	1
T( $^\circ K$ ), adiabatic temperature	1659	1502	1343	1182	1023	863

## Equilibrium Hydrazine Decomposition

If we allowed "infinite" time for the reaction, hydrazine products would reach an equilibrium with little ammonia left (depending on pressure). The product,  $N_2$ ,  $H_2$ ,  $NH_3$ , must then satisfy

$$\frac{P_{NH_3}}{P_{N_2}^{1/2} P_{H_2}^{3/2}} = K_p(T);$$

$$K_p \approx 1.089 \times 10^{-6} e^{\frac{6289}{T}} \text{ (atm}^{-1}\text{)} \quad (P\text{'s in atm)}$$

and the pressure is

$$P = P_{NH_3} + P_{N_2} + P_{H_2}$$

To conserve moles of H and N, starting from (arbitrarily) 3 moles of  $N_2H_4$ , we must have

$$\left. \begin{array}{l} \text{H: } 3n_{NH_3} + 2n_{H_2} = 3 \times 4 = 12 \\ \text{N: } n_{NH_3} + 2n_{N_2} = 3 \times 2 = 6 \end{array} \right\} \text{dividing, } \frac{3P_{NH_3} + 2P_{H_2}}{P_{NH_3} + 2P_{N_2}} = 2$$

Define

$$y = \frac{P_{NH_3}}{P} \quad (\text{ammonia mole fraction}).$$

Then

$$\frac{3y + 2P_{H_2}/P}{y + 2P_{N_2}/P} = 2$$

and

$$y + \frac{P_{H_2}}{P} + \frac{P_{N_2}}{P} = 1$$

Solving,

$$\frac{P_{H_2}}{P} = \frac{2}{3} \left( 1 - \frac{5}{4} y \right)$$

$$\frac{P_{N_2}}{P} = \frac{1}{3} \left( 1 - \frac{1}{2} y \right)$$

and substituting into the equilibrium law,

$$\frac{y}{\left[\frac{1}{3}\left(1 - \frac{1}{2}y\right)\right]^{1/2} \left[\frac{2}{3}\left(1 - \frac{5}{4}y\right)\right]^{3/2}} = K_p P$$

$$\frac{y}{\left(1 - \frac{1}{2}y\right)^{1/2} \left(1 - \frac{5}{4}y\right)^{3/2}} = \left(\frac{1}{3}\right)^{1/2} \left(\frac{2}{3}\right)^{3/2} PK_p(T) \equiv K_y$$

So, given P and T, we can solve this for

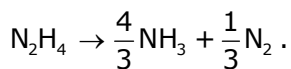
$$y = \frac{P_{\text{NH}_3}}{P}.$$

But T itself must be consistent with energy conservation

$$\frac{4}{3}(1-x)h_{\text{NH}_3}(T) + \frac{1+2x}{3}h_{\text{N}_2}(T) + 2xh_{\text{H}_2}(T) = h_{\text{N}_2\text{H}_4}$$

where  $h_{\text{N}_2\text{H}_4}$  would be 12.0 Kcal/mol if we start from liquid hydrazine at 298K, or it could include the external heating energy due to an electrical heater, as in the case of an Electrothermally Augmented thruster (in fact, in this case the equilibrium assumption is realistic, given the long residence time in the heater, and the higher temperature).

Now x is the fraction of  $\text{NH}_3$  decomposed after the initial fast reaction



To relate it to y, which is the mole fraction of  $\text{NH}_3$  in the final products, we write

$$y = \frac{\frac{4}{3}(1-x)}{\frac{4}{3}(1-x) + \frac{1+2x}{3} + 2x} = \frac{4(1-x)}{5+4x}$$

or

$$\boxed{x = \frac{4-5y}{4(1+y)}}$$

(notice for  $x=0$  we have  $y = \frac{4}{5}$ , i.e.  $\frac{1}{5}$  of the products is  $\text{N}_2$  while for  $x=1$ ,  $y=0$ ).

So, to complete the computation, we could iterate as follows:

- (1) Given P, guess T

(2) Compute  $K_p(T), K_y(T, P), h_{\text{NH}_3}(T), h_{\text{N}_2}(T), h_{\text{H}_2}(T)$

(3) Solve

$$\frac{y}{\left(1 - \frac{y}{2}\right)^{1/2} \left(1 - \frac{4}{5}y\right)^{3/2}} = K_y \text{ for } y$$

(4) Calculate  $x = \frac{4 - 5y}{4(1 + y)}$

(5) Calculate  $h_{\text{prods.}} = \frac{4}{3}(1 - x)h_{\text{NH}_3} + \frac{1 + 2x}{3}h_{\text{N}_2} + 2xh_{\text{H}_2}$

and the "error"  $h_{\text{prods.}} - h_{\text{N}_2\text{H}_4}$

(6) Use this error to generate a new T guess, go back to (2)

Some results (with no external heating)

P(atm)	$y = \frac{P_{\text{NH}_3}}{P}$	T(K)
2	0.00098	864.8
5	0.0024	867.3
10	0.0046	871.3
20	0.0086	878.4
50	0.0185	895.5
100	0.0306	916.3
200	0.0479	945.0

which, indeed, shows minimal  $\text{NH}_3$  present

For propulsion purposes, the important thing is not T, but  $I_{\text{sp}}$ . This depends also on the molecular weight of the gas (and somewhat on  $\gamma$ ); since the gas gets lighter as  $\text{NH}_3$  decomposes, this compensates for the lower T, and  $I_{\text{sp}}$  is very insensitive to x for  $x < 0.4$ . Assuming frozen flow (constant  $\gamma$ , constant M), and a pressure ratio  $P_e/P_0$ ,

the exit velocity is

$$u_e = \sqrt{2 \frac{\gamma}{\gamma - 1} \frac{R}{M} T_0 \left[ 1 - \left( \frac{P_e}{P_0} \right)^{\frac{\gamma}{\gamma - 1}} \right]}$$

$$M = \frac{17x \frac{4}{3}(1 - x) + 28 \frac{1 + 2x}{3} + 2x \cdot 2}{\frac{4}{3}(1 - x) + \frac{1 + 2x}{3} + 2x}$$

$$M = \frac{96}{5 + 4x}$$

and the area ratio is

$$\frac{A_e}{A^*} = \sqrt{\frac{\gamma-1}{2}} \left( \frac{2}{\gamma+1} \right)^{\frac{\gamma+1}{2}} \frac{1}{\left( \frac{P_e}{P_0} \right)^{1/\gamma} \sqrt{1 - \left( \frac{P_e}{P_0} \right)^{\frac{\gamma-1}{\gamma}}}}$$

and so, in vacuum

$$I_{sp} = \frac{F}{\dot{m}g} = \frac{\dot{m}u_e + P_e A_e}{\dot{m}g} = \frac{u_e}{g} + \frac{P_e A_e}{\dot{m}g} = \frac{u_e}{g} + \frac{P_e}{P_0} \frac{A_e}{A^*} \frac{c^*}{g}$$

with

$$\dot{m} = \frac{P_0 A^*}{c^*}, c^* = \frac{\sqrt{R/M T_0}}{T}, T = \sqrt{\gamma} \left( \frac{2}{\gamma+1} \right)^{\frac{\gamma+1}{2}}$$

Take  $P_e/P_0=0.0012$  (about  $A_e/A^*=50$ ).

Using chamber composition (pretty good),

$$M = \frac{17 \frac{4}{3}(1-x) + 28 \frac{1+2x}{3} + 4x}{\frac{4}{3}(1-x) + \frac{1+2x}{3} + 2x} = \frac{68(1-x) + 28(1+2x) + 12x}{4(1-x) + 1 + 2x + 6x} = \frac{96}{5+4x}$$

1.986

$$\gamma = \frac{\frac{4}{3}(1-x)(12.35 + 2 \times 0.9830) + \frac{1+2x}{3}(7.75 + 2 \times 0.1830) + 2x(6.6 + 2 \times 0.3670)}{\frac{4}{3}(1-x)(10.36 + 1.9660) + \frac{1+2x}{3}(5.76 + 0.3660) + 2x(4.61 + 0.7340)}$$

$$x = 0.4 \rightarrow \theta = 1.343$$

$$\gamma = \frac{\frac{4}{3} 0.6(12.35 + 1.966 \times 1.343) + \frac{1.8}{3}(7.75 + 0.366 \times 1.343) + 0.8(6.6 + 0.7340)}{0.8(10.36 + \_\_\_) + 0.6(5.76 + \_\_\_) + 0.8(4.61 + \_\_\_)}$$

$$\gamma = 1.234 \quad (\text{for comparison, at the throat } T, \gamma^* = 1.238)$$

As a practical matter, one wants  $T_0$  as low as possible if the performance is acceptable. A very common choice is  $x = 0.4 \rightarrow I_{sp} \approx 250$  sec. (ideal)

