

## Session 12 : Monopropellant Thrusters

Electrothermal augmentation of chemical rockets was the first form of electric propulsion applied in space vehicles. In its original implementation, resistojets were used to improve the performance of regular hydrazine ( $\text{N}_2\text{H}_4$ ) thrusters in geostationary satellites. The motivation for this important application is relevant to the development of electric propulsion and will be discussed in detail in this lecture. We start by reviewing the fundamentals of hydrazine monopropellant propulsion.

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  $\text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 2\text{H}_2$ , but a more exothermic one such as  $2\text{N}_2\text{H}_4 \rightarrow 2\text{NH}_3 + \text{N}_2 + \text{H}_2$ .

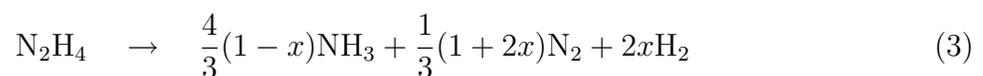
When catalyzed either by an oxide or by a hot platinum surface,  $\text{N}_2\text{H}_4$  decomposes. Since at low temperatures ammonia,  $\text{NH}_3$ , is stable, the preferred end products would be  $\text{NH}_3 + \text{N}_2$ :



However, this is a very exothermic reaction, and the equilibration temperature ( $T$ ) would be 1650 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 an intermediate  $T$ , since the latter reaction is endothermic. In practice reaction (1) is very fast (less than 1 msec) if catalyzed, while (2) is slow. Hence, for small decomposition chambers and high flow rates, when the residence time  $\rho v/\dot{m}$  is short, reaction (2) 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  $\text{N}_2\text{H}_4$  at 298 K),

$$h_{\text{N}_2\text{H}_4}(\ell, 298\text{K}) = \frac{4}{3}(1-x)h_{\text{NH}_3} + \frac{1}{3}(1+2x)h_{\text{N}_2} + 2xh_{\text{H}_2} \quad (4)$$

The respective molar enthalpies (kcal/mol) can be fitted by,

$$\begin{aligned} h_{\text{NH}_3}(T) &= -16.83 + 12.35\theta + 0.983\theta^2 \\ h_{\text{N}_2}(T) &= -2.83 + 7.75\theta + 0.183\theta^2 \\ h_{\text{H}_2}(T) &= -1.967 + 6.6\theta + 0.367\theta^2 \end{aligned} \quad (5)$$

where  $\theta = \frac{T}{1000\text{K}}$ . These expressions are valid in the range  $0.3 < \theta < 4$ . The specific heat is  $c_p(\text{cal/mol K}) = \frac{dh}{d\theta}$ .

The value of the enthalpy of liquid hydrazine at standard conditions can be found from tables,  $h_{\text{N}_2\text{H}_4}(\ell, 298\text{K}) = 12 \text{ kcal/mol}$ . We can now solve for the temperature at various arbitrary values of  $x$ ,

$$\theta = \frac{\sqrt{139.3 - 20.75x + 8.45x^2} - (9.525 + 0.95x)}{1.372 - 0.455x} \quad (6)$$

Results from Eq. (6) are shown in the table below:

$x$ (fraction of $\text{NH}_3$ decomposed)	0	0.2	0.4	0.6	0.8	1
$T$ (K) adiabatic temperature	1659	1502	1343	1182	1023	863

Up to this point, the ammonia decomposition fraction has been considered as a free parameter. In practice, it will depend on residence time and operating conditions, in particular the chamber pressure. If we assume that residence time is long enough to allow for *infinite* time for the decomposition reaction, hydrazine products would reach an equilibrium with some ammonia left (depending on pressure). From the law of mass action, the products must satisfy,

$$\frac{p_{\text{NH}_3}}{p_{\text{N}_2}^{1/2} p_{\text{H}_2}^{3/2}} = K_p(T) \quad (7)$$

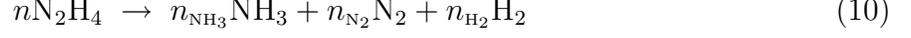
where the equilibrium constant is approximated by (pressures in atm),

$$K_p(T) \approx 1.089 \times 10^{-6} e^{\frac{6289}{T}} \quad \text{in atm}^{-1} \quad (8)$$

and in terms of partial pressures we have,

$$p = p_{\text{NH}_3} + p_{\text{N}_2} + p_{\text{H}_2} \quad (9)$$

Writing the reaction in terms of partial molar densities,



we impose species conservation,

$$\begin{aligned} \text{for H} &\rightarrow 4n = 3n_{\text{NH}_3} + 2n_{\text{H}_2} \\ \text{for N} &\rightarrow 2n = n_{\text{NH}_3} + 2n_{\text{N}_2} \end{aligned} \quad (11)$$

or in terms of the partial pressures, since  $p = nkT$ ,

$$2 = \frac{3p_{\text{NH}_3} + 2p_{\text{H}_2}}{p_{\text{NH}_3} + 2p_{\text{N}_2}} \quad (12)$$

Eqs. (7-9) and (12) constitute a system of four equations and four unknowns, i.e., the partial pressures and temperature. We solve this system by defining the ammonia mole fraction,

$$y = \frac{p_{\text{NH}_3}}{p} \quad (13)$$

After some manipulation, these equations can be written as,

$$\begin{aligned} \frac{p_{\text{NH}_3}}{p} &= \frac{1}{3} \left(1 - \frac{y}{2}\right) \\ \frac{p_{\text{H}_2}}{p} &= \frac{2}{3} \left(1 - \frac{5y}{4}\right) \\ K_p(T) &= \frac{y/p}{(p_{\text{N}_2}/p)^{1/2} (p_{\text{H}_2}/p)^{3/2}} \end{aligned} \quad (14)$$

We also write the mol fraction Eq. (13) in terms of  $x$ ,

$$y = \frac{\frac{4}{3}(1-x)}{\frac{4}{3}(1-x) + \frac{1}{3}(1+2x) + 2x} = \frac{4(1-x)}{5+4x} \quad (15)$$

or, solving for  $x$  in terms of  $y$ ,

$$x = \frac{1-5y/4}{1+y} \quad (16)$$

Given some pressure  $p$  and an initial guess for the temperature  $T$ , we find  $y$  and  $x$ . At this point we need to verify that the temperature used in this calculation is consistent with the energy balance in Eq. (4). In all likelihood the temperature from Eq. (4) will not coincide with the initial guess, so we need to perform a few iterations of this process. In practice, selecting the adiabatic temperature from the energy balance as initial guess for each iteration suffices to guarantee quick convergence.

The following table shows some results using this procedure as a function of pressure.

$p$ (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

In all these cases we observe that ammonia is near to complete decomposition if allowed to reach equilibrium conditions. If this result is not desirable in a thruster, then the only additional knob to control decomposition is residence time, so in many instances the geometry of the thruster is essential to determine the performance.

Now, for propulsion purposes, the important thing is not the adiabatic temperature, but the  $I_{sp}$ . This depends also on the molecular weight of the gas; since the gas gets lighter as  $\text{NH}_3$  decomposes, this compensates for the lower  $T$ , and  $I_{sp}$  is very insensitive to  $x$ , for  $x < 0.4$ .

$$I_{sp} = \frac{F}{\dot{m}g} = \frac{\dot{m}u_e + p_e A_e}{\dot{m}g} = \frac{u_e}{g} + \frac{p_e A_e c^*}{p_0 A_t g} \quad (17)$$

where the characteristic velocity is defined as usual,

$$c^* = \frac{p_0 A_t}{\dot{m}} = \frac{\sqrt{R/M T_0}}{\Gamma(\gamma)} \quad \text{with} \quad \Gamma(\gamma) = \sqrt{\gamma} \left( \frac{2}{\gamma+1} \right)^{\frac{\gamma+1}{2(\gamma-1)}}$$

Assuming frozen flow, and a pressure ratio  $p_e/p_0$ , the exit velocity is,

$$u_e = \sqrt{\frac{2\gamma}{\gamma-1} \frac{R}{M} T_0 \left[ 1 - \left( \frac{p_e}{p_0} \right)^{\frac{\gamma-1}{\gamma}} \right]} \quad (18)$$

The molecular mass is obtained with a weighted average,

$$M = \frac{M_{\text{NH}_3} \frac{4}{3}(1-x) + M_{\text{N}_2} \frac{1}{3}(1+2x) + M_{\text{H}_2} 2x}{\frac{4}{3}(1-x) + \frac{1}{3}(1+2x) + 2x} = \frac{96}{5+4x} \quad (19)$$

A similar procedure can be used to compute the weighted average for the specific heat, and from here the ratio of specific heats  $\gamma = \gamma(x)$ .

The area ratio is,

$$\frac{A_e}{A_t} = \sqrt{\frac{\gamma - 1}{2}} \left( \frac{2}{\gamma + 1} \right)^{\frac{\gamma+1}{2(\gamma-1)}} \left( \frac{p_e}{p_0} \right)^{-\frac{1}{\gamma}} \left[ 1 - \left( \frac{p_e}{p_0} \right)^{\frac{\gamma-1}{\gamma}} \right]^{1/2} \quad (20)$$

The following page contains the results from these calculations for a pressure ratio  $p_e/p_0 = 0.0012$ , corresponding to an area ratio of about  $A_e/A_t = 50$ .

As a practical matter, one wants  $T_0$  as low as possible if the performance is acceptable. A very common choice is  $x = 0.4$  for a specific impulse of about 250 sec.

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