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Metallic Hydrogen: The Most Powerful Rocket Fuel Yet to Exist

Isaac F. Silvera¹ and John W. Cole²

¹Lyman Laboratory of Physics, Harvard University, Cambridge MA 02138

²NASA MSFC, Retired, Huntsville, AL 35801

E-mail: silvera@physics.harvard.edu

Abstract. Wigner and Huntington first predicted that pressures of order 25 GPa were required for the transition of solid molecular hydrogen to the atomic metallic phase. Later it was predicted that metallic hydrogen might be a metastable material so that it remains metallic when pressure is released. Experimental pressures achieved on hydrogen have been more than an order of magnitude higher than the predicted transition pressure and yet it remains an insulator. We discuss the applications of metastable metallic hydrogen to rocketry. Metastable metallic hydrogen would be a very light-weight, low volume, powerful rocket propellant. One of the characteristics of a propellant is its specific impulse, I_{sp} . Liquid (molecular) hydrogen-oxygen used in modern rockets has an I_{sp} of ~460s; metallic hydrogen has a theoretical I_{sp} of 1700 s! Detailed analysis shows that such a fuel would allow single-stage rockets to enter into orbit or carry economical payloads to the moon. If pure metallic hydrogen is used as a propellant, the reaction chamber temperature is calculated to be greater than 6000 K, too high for currently known rocket engine materials. By diluting metallic hydrogen with liquid hydrogen or water, the reaction temperature can be reduced, yet there is still a significant performance improvement for the diluted mixture.

Introduction

Production of metallic hydrogen in the laboratory is one of the great challenges of high-pressure physics. Not only is it predicted to have fascinating fundamental properties but also revolutionary applied properties. In this paper we discuss the progress towards producing metallic hydrogen and an application to rocketry as a powerful propellant.

Over 70 years ago Wigner and Huntington [1] predicted that if solid molecular hydrogen was compressed to a pressure of 25 GPa it would have a dissociative transition from a molecular solid to an atomic solid with a half-filled conduction band so that it would be metallic. Later, Ashcroft [2] predicted that the putative metallic hydrogen might be a room temperature superconductor. It was also predicted by Ramaker, Kumar, and Harris [3] that high pressure molecular hydrogen would become metallic; a recent publication predicts high temperature superconductivity for the molecular phase [4]. Brovman, Kagan, and Kholas [5] showed that hydrogen would be a metastable metal with a potential barrier of ~1 eV. That is, if the pressure on metallic hydrogen were relaxed, it would remain in the metallic phase, just as diamond is a metastable phase of carbon. However, Salpeter [6] showed that the metastability time of hydrogen might be short due to a tunnelling mechanism in which atoms on the atomic lattice tunnel into molecular states. Since metallic hydrogen is yet to be produced in the laboratory, none of these ideas have been tested.

If metallic hydrogen is a metastable substance and can be economically produced in the laboratory then it would be the most powerful chemical rocket propellant in existence. In the past such assertions were made because of the large energy of recombination and the very light mass of hydrogen; in this paper we demonstrate the advantages using detailed calculations. In rocketry one of the important attributes of a propellant is its specific impulse I_{sp} , related to the thrust (see definition ahead). For example, (molecular) hydrogen-oxygen, currently the most powerful propellant, with an

$I_{sp} \approx 460$ s, is the fuel for the main engine on the Space Shuttle. A fuel with an increase of 50 s would have a significant impact on the payload of the Shuttle. Metallic hydrogen has been cited as a fuel that could bring important improvements to rocketry. Carrick [7] calculated the I_{sp} of metallic hydrogen and found a value of ~ 1400 s. In addition to the I_{sp} advantage, metallic hydrogen is ~ 10 times denser than molecular hydrogen and probably would not need cooling as a cryogenic fuel, further reducing the size or increasing the payload.

We decided to carry out a realistic analysis of the impact that metastable metallic hydrogen would have on the design of rockets propelled by this fuel using advanced codes for the analysis. With pure metallic hydrogen as the fuel, it was found that the temperatures in the combustion chamber would be too high for current construction materials used in rocket engines. We then decided to dilute the metallic hydrogen to lower the combustion temperatures and analyzed mixtures of metallic hydrogen with molecular hydrogen and metallic hydrogen with water. Even with this dilution, revolutionary improvements would be made in rocketry, for example, a single stage to orbit. In the following section of this paper we discuss the current status of efforts to produce metallic hydrogen using high-pressure techniques. We then discuss rocket engines and conclude with designs of metallic hydrogen fuelled launch vehicles.

The Status of Experiments to Produce Metallic Hydrogen

The original predicted pressure of 25 GPa for the metallization of hydrogen was made early in the development of the quantum mechanics for many-particle systems. Experimentally this pressure has been exceeded by more than an order of magnitude and hydrogen remains in the non-metallic molecular phase. Studies have been carried out on hydrogen and its isotope deuterium, as well as hydrogen deuteride. There are two methods of producing high pressures, static and dynamic. Almost all modern studies on solid hydrogen at static high pressures have been carried out in diamond anvil cells (DACs). Shockwave experiments achieve high pressures for very short periods of time, but the temperatures are thousands of degrees K and the hydrogen samples are in the liquid phase. In a dynamic shockwave experiment, Weir, Mitchell, and Nellis [8] observed liquid hydrogen to enter a conductive state, believed to be metallic at pressures of 140 GPa and temperatures of 2000 to 3000 K.

The first very high-pressure DAC experiments were carried out at low temperatures and two new phases were discovered. If we focus on para-hydrogen (or ortho-deuterium) then at lower pressures and down to $T=0$ K, the solids are in the hexagonal close packed (hcp) phase and the molecules are in spherically symmetric quantum mechanical states. At high pressure (110 GPa for hydrogen; 28 GPa for deuterium) a phase transition to the so-called broken symmetry phase, or BSP, takes place in which the single-particle molecular states are no longer spherically symmetric and the molecules orientationally order their symmetry axes along crystalline directions. At a still higher pressure of ~ 150 GPa another transition takes place to the so-called A-phase. This phase is also a non-conducting orientationally ordered phase. A phase diagram from Cui et al [9] for ortho-deuterium is shown in figure. 1. The three phases discussed are sometimes referred to as I, II, and III.

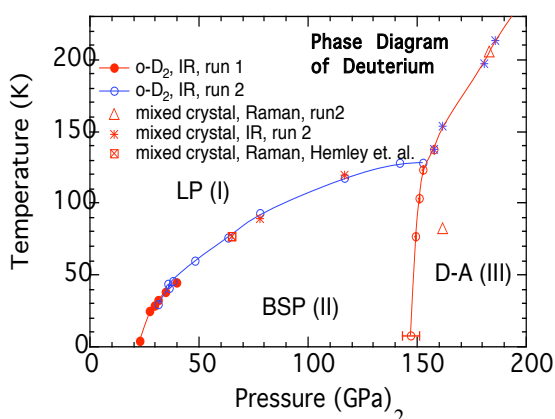


Figure 1. The high pressure phase diagram of ortho-deuterium showing the low pressure-LP, BSP and A phases.

The highest pressures on hydrogen, in the 300 to 400 GPa range, have been obtained by two groups. Narayana et al [10] achieved pressures in the region of 340 GPa stating that hydrogen remained transparent. Loubeyre, Occelli, and LeToullec [11] found hydrogen to darken at 320 GPa as a band gap was closed through the visible. Both groups found that hydrogen was still in the molecular phase. Extrapolations of data from Loubeyre, Occelli, and LeToullec indicate that the transition pressure is above 4.5 Mbar. Some inconsistencies, as a result of the two groups using different pressure scales, have been explained by Silvera [12].

Since the work of Wigner and Huntington there have been numerous calculations of the critical pressure for the dissociative transition from molecular to solid atomic metallic hydrogen; many of these results have been reviewed (Silvera [13]). These calculations utilize various techniques such as density functional theory, quantum Monte Carlo, etc. Although quantum chemistry calculations have been developed to a high degree of sophistication, and in general, there is a close correlation between theory and experiment, this is not the case for hydrogen. Phase transition calculations that seek the structure with the lowest lattice energy have difficulty handling the zero-point energy contribution to the total energy and zero-point energy is very important in hydrogen. As a result, the predicted critical transition pressures have an enormous variation, from as low as 0.25 Mbar to over 20 Mbar, while recent predictions are in the 400 to 600 GPa range.

In recent years a new pathway along the melting line has been under investigation. Scandolo [14] predicted that at high pressure hydrogen would have a negative slope in its melting line. This was followed by a detailed two-phase molecular dynamics study by Bonev et al [15] who showed that hydrogen should indeed have a peak in its melting line. They extrapolated their curve with a negative slope to very high pressures and zero Kelvin, indicating that hydrogen may melt from the molecular phase into the metallic phase, so that in the 400 to 600 GPa range hydrogen would be an atomic liquid at $T=0$ K, shown in figure 2. Attacalite and Sorella [16] have calculated a point at high pressure and lower temperatures that is in agreement with the extrapolation. Babaev, Sudbo, and Ashcroft [17] considered the possibility of two component superconductivity with itinerant electrons and protons.

On the experimental side, measurements of the melting line by Datchi et al [18] and Gregoryanz et al [19] found curvature in the line, indicating that a peak might exist. Experimental challenges prevented them from extending the melt line to higher pressures and temperatures to investigate this possibility. Recently Deemyad and Silvera [20] used pulsed laser heating and found a sharp peak in the melt line at 64.7 GPa and 1050 K, shown in figure 3. Eremets and Trojan [21] have recently

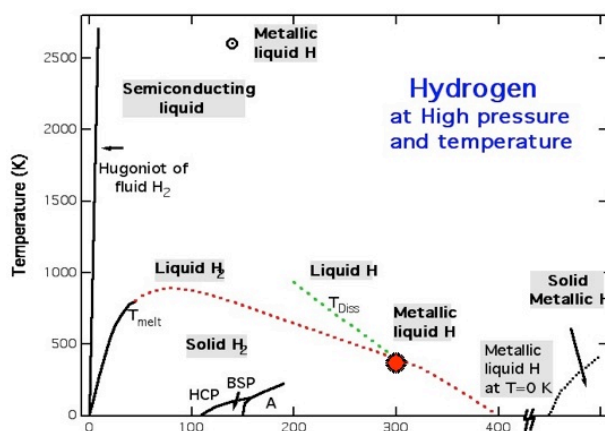


Figure 2. Phase diagram of hydrogen showing extrapolation of the melting line (below 700 K) to very high pressure. The melting line of Bonev *et al.* was carried out to 700 K. The recent work of Attacalite and Sorella (filled circle) confirms the extrapolation to 400 K.

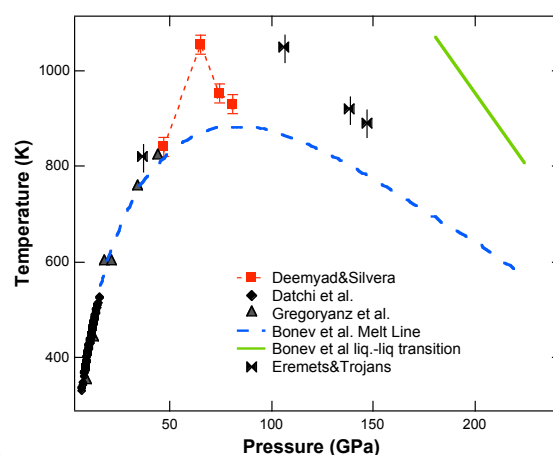


Figure 3. Experimental measurements of the melting line, compared to theory. The solid line (upper right, green) is the liquid-liquid molecular to atomic line.

extended the melt line to higher pressures and confirm the existence of a peak. Efforts to study hydrogen and its isotopes at still higher pressures, aimed at the transition to metallization, continue.

Rocket Engines

A liquid rocket engine is fundamentally a quite simple device. Liquid fuel and oxidizer are injected into a reaction chamber where combustion releases the chemical energy producing a hot gas. The hot combustion products exit the chamber at fairly high pressure through a throat and then expand out of a nozzle. In **gas dynamical** terms as the gas expands the random motion of the gas particles in the combustion chamber are converted via collisions with each other and the nozzle walls into directed motion in the direction opposite of the acceleration of the rocket. In the moving frame of the expanding gas the temperature (random component of the molecular motion) decreases. The expansion can only proceed at the speed of sound, which is a function of temperature. Constrained by the nozzle walls the moving gas expands at the speed of sound relative to the local speed in the gas. So the expanding gases push the gases in front of them that are also expanding, pushing the gases in front of them, etc., without locally exceeding the speed of sound constraint. This result is an exhaust that can be very supersonic and directed optimizing the transfer of momentum to the rocket. The kinetic energy from the exhaust represents the energy that can be obtained from the propellant by the engine for acceleration. Lighter molecular weight exhaust products provide higher exhaust velocities for a given initial chamber temperature.

The fuel and oxidizer must be injected into the chamber at a pressure higher than the pressure in the chamber. In large rocket engines this pressure is obtained by pumps powered by turbines that use some of the vehicle fuel and oxidizer as their energy source. Some rocket engines dump the turbo-pump exhaust overboard so this propellant does not directly contribute to the engine thrust. More advanced engines operate the turbo-pumps at very high pressure and the high-pressure exhaust is injected with the fuel into the combustion chamber. This staged combustion approach allows most of the turbo-pump energy to be recovered improving the thrust and I_{sp} . Liquid rocket engine design techniques have progressed to the point that only minor improvements in performance are now achieved. These improvements come from lighter weight high temperature materials and from computer aided design and computational fluid dynamics to design more efficient pumps and injectors. First-stage propellants are generally liquid oxygen and kerosene which has about half the energy content of the liquid oxygen and hydrogen upper stage propellants. Hydrazine and nitrogen tetroxide provide slightly more specific energy than liquid oxygen and kerosene, as does liquid oxygen and methane. A safe and affordable propellant with very high specific energy and with light-weight exhaust products would enable substantial improvements in rocket performance.

Metallic Hydrogen Launch Vehicle Application

The metastability of metallic hydrogen depends on temperature and pressure. Above some temperature there will be sufficient thermal energy in the atomic lattice for the atoms to rise above the potential barrier and recombine into hydrogen molecules, releasing the energy of recombination, 216 MJ/kg (note: the dissociation energy of a hydrogen molecule is 4.68 eV). This is more than twenty times the specific energy released by the combustion of hydrogen and oxygen in the Space Shuttle's main engines, 10 MJ/kg. Because of this very large potential specific energy, it is interesting to explore the possible use of metallic hydrogen as an energy source for rocket powered launch vehicles. Since metallic hydrogen has not yet been produced and the material has only been characterized theoretically, some assumptions must be made to investigate its potential use in a rocket vehicle. We assume that metallic hydrogen is a metastable solid or liquid at ambient conditions, that it is compatible with launch vehicle propulsion environments (vehicle vibrations, pumps, valves, etc.), and that it can be safely and affordably produced and handled in large quantities. We also assume that it has a density of 0.7 gm/cm³ (liquid H₂ density is about 0.07 gm/cm³) and that **its** metastability is overcome at around 1000 K for 40 bar pressure.

We have considered pure metallic hydrogen and diluted mixtures, to reduce the combustion temperature. Diluting the atomic hydrogen with water or with molecular hydrogen will reduce the chamber temperature to reasonable material limits while still delivering a high specific energy, E_{sp} . A rocket engine converts the energy available from the fuel into the kinetic energy of the exhaust,

$$E_{sp} = E/m_f = \frac{1}{2} v_{ex}^2 \quad (1)$$

where v_{ex} is the exhaust velocity, E is the available kinetic energy in the fuel, and m_f is the propellant mass. Rocket scientists prefer to use specific impulse, I_{sp} , rather than specific energy when discussing rocket engines. Specific impulse represents the number of seconds that a thrust of one kilogram of force (**Newtons**) can be sustained by one kilogram mass of propellant, and is related to the square root of the specific energy,

$$I_{sp} = F/\dot{m}g_0 = \dot{m}v_{ex}/\dot{m}g_0 = v_{ex}/g_0 = \sqrt{2E_{sp}/g_0}. \quad (2)$$

Here F is thrust, \dot{m} is propellant flow rate, and g_0 is the gravitational constant from the kilogram of force definition.

We have used the NASA Glenn Chemical Equilibrium Calculation (CEC) [22] to evaluate the properties of the rocket engine. We find that a reaction chamber filled with atomic hydrogen at 100 atm of pressure will reach recombination/dissociation equilibrium temperatures much greater than 7000 K where ~50% of the hydrogen remains dissociated. This would provide a theoretical specific impulse of 1700 s, but clearly, the temperature is higher than any known chamber material can withstand. Even at 40 atm pressure at equilibrium a temperature of ~6700 K will develop, far above the melting point of available rocket engine materials.

Diluting the atomic hydrogen in the rocket chamber with water or with molecular hydrogen will reduce the chamber temperature, T_c , to reasonable material limits while still delivering a high specific impulse. To achieve chamber temperatures between $T_c = 3500 - 3800$ K water diluents will provide $I_{sp} = 460- 540$ seconds and hydrogen diluents will provide $I_{sp} = 1030 - 1120$ seconds. For comparison, as mentioned earlier, the Space Shuttle main engines provide an $I_{sp} \sim 460$ seconds.

The next step in conceptualizing metallic hydrogen propelled launch vehicles is to determine the size of each stage required to deliver a payload to a desired orbit or location. For this we need the rocket equation. The momentum carried away by a small amount of rocket exhaust provides a reactive thrust on the vehicle that adds a little momentum to the vehicle. From conservation of momentum, the changes in momentum must balance:

$$v_{ex} dm + m dv_v = 0, \quad (3)$$

where dm is the differential vehicle mass (exhaust), m is the vehicle instantaneous mass, and dv_v is the differential vehicle velocity. Integration of equation 3 yields the Tsiolkovsky rocket equation [23] which can be written

$$\frac{m_i}{m_0} = e^{-\Delta v/v_{ex}} = e^{-\Delta v/g_0 I_{sp}} \quad (4)$$

where m_0 is the initial mass, m_i is the injected mass (stage dry mass plus stage payload at stage burn out), and Δv is the change in ideal velocity (including velocity losses from drag, gravity, steering, etc.). Equation 4 can be used to determine the mass ratios of each stage given a mission Δv

requirement and an I_{sp} for each stage. Propellant densities and mixture ratios permit the individual tank sizes to be determined with appropriate margins for engineering and safety.

Because of the limited specific energy available from current propellants there are no existing launch vehicles that can reach orbit with a single stage. A single stage to orbit would greatly reduce complications and cost of such missions. Recently we calculated the size of several single-stage to orbit launch vehicles that deliver 25 MT (metric tons) of payload to low earth orbit with a $\Delta v = 9.2$ km/s, figure 4 [24]. The vehicle is a little smaller than the Shuttle but significantly lighter in weight (see figure 4) and delivers the payload with only one stage. The metallic hydrogen is carried in a small spherical tank inside the liquid hydrogen diluents tank.

In another analysis we examined launch vehicles with two stages that deliver 35 MT of cargo to the lunar surface requiring a $\Delta v = 16.4$ km/s, figure. 5. For this launch vehicle the 1st stage is cooled with water diluents and provides 45% of the mission Δv , the 2nd stage is cooled with hydrogen diluents, and both stages are 7.5 m in diameter. With a vehicle that is slightly taller, but lighter than the Shuttle (shown only for size comparison), a much larger payload is delivered to a much more challenging destination. Once again, because of propellant specific energy limits there are no current two-stage vehicles that can land payloads on the lunar surface.

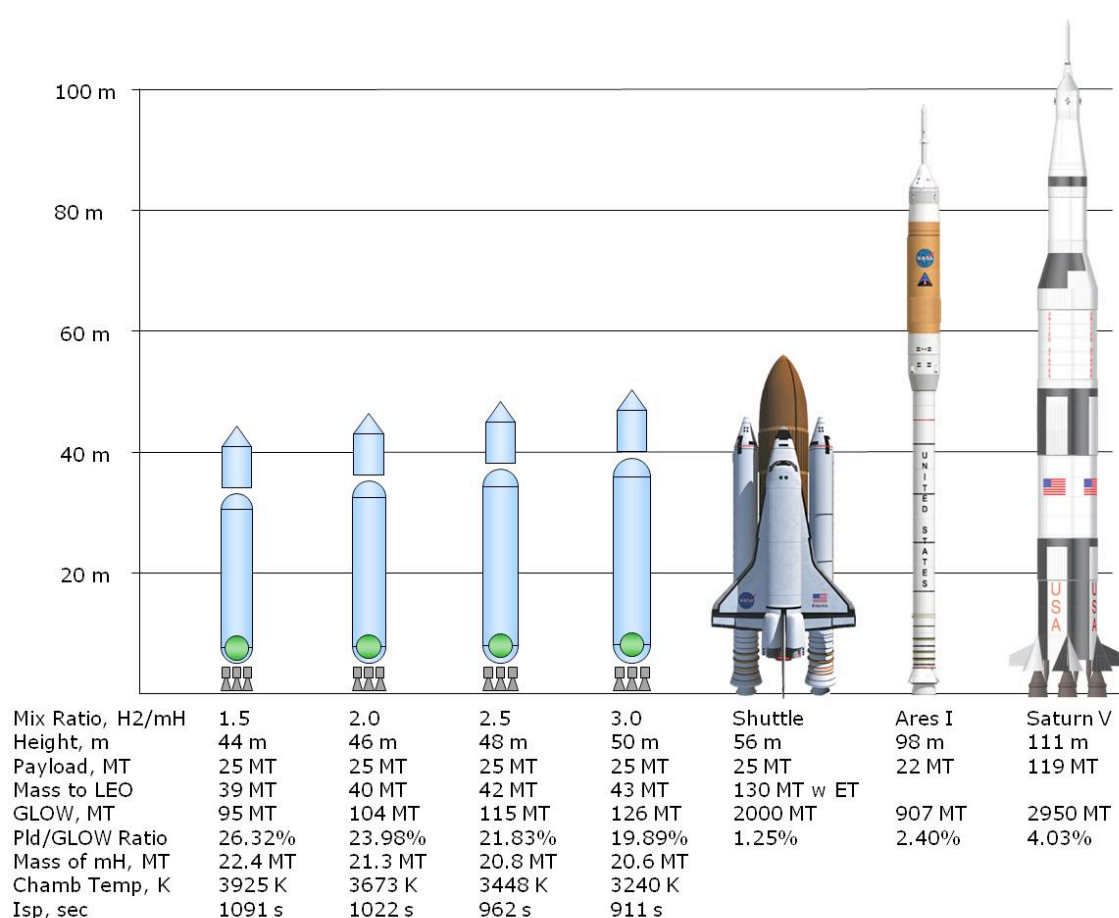


Figure 4. Sketch depicting the sizes of liquid hydrogen cooled metallic hydrogen single-stage to orbit (SSTO) launch vehicles that can deliver 25 metric tons to low earth orbit (LEO), compared to other vehicles. Important properties are tabulated, including the gross lift-off weight (GLOW).

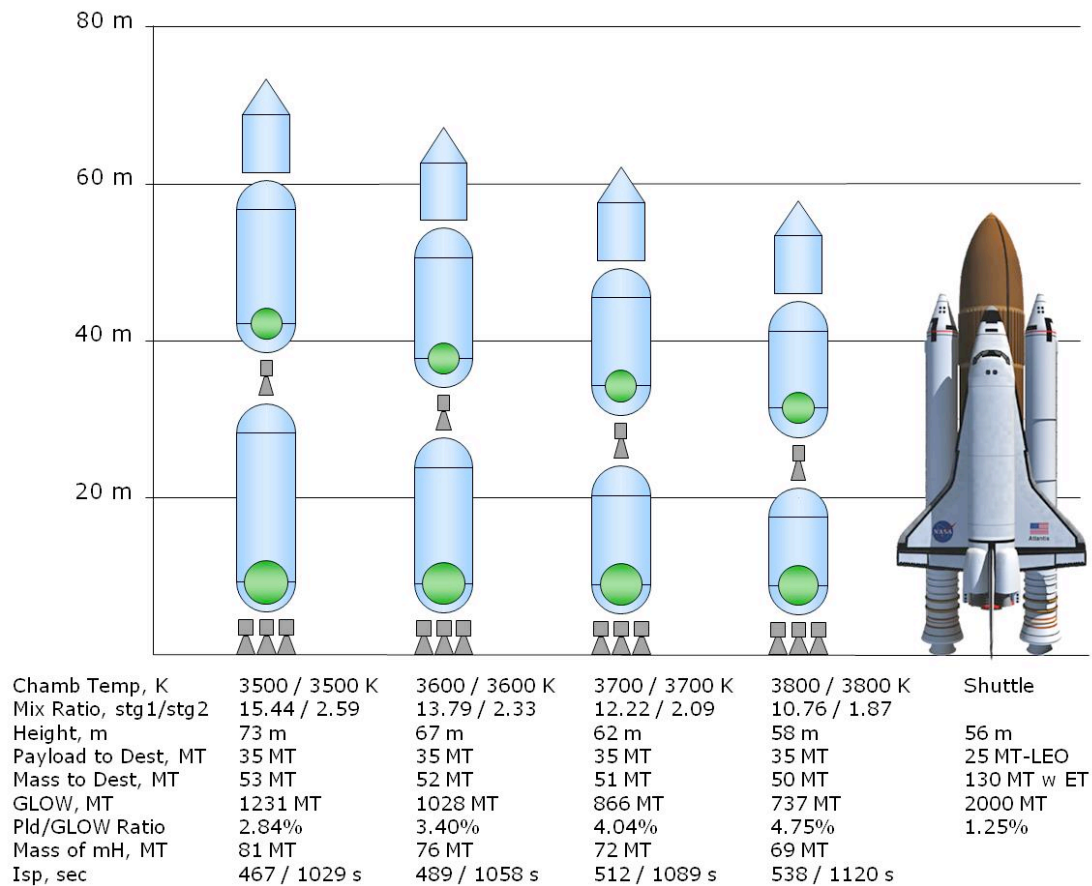


Figure 5. Two stage launch vehicle concepts that deliver a 35 metric ton payload plus an empty 2nd Stage to the Lunar Surface. Chamber temperatures between these concepts vary from 3500 K to 3800 K. The metallic hydrogen for the 1st stage is diluted with water, and for the 2nd stage with liquid hydrogen.

Yet another analysis examined two-stage launch vehicles that deliver 30 MT into a geosynchronous transfer orbit (GTO) that will carry the payload to geosynchronous orbit altitude but not provide orbit circularization or plane change to achieve an equatorial inclination. The vehicle and engine characteristics are the same as the lunar cargo mission except for the payload mass, the mission $\Delta v = 11.7$ km/s, the vehicle diameter of 5.5 m and the resulting vehicle height of about 53 m. The initial mass for the vehicle concepts ranges from 242 to 323 MT. For comparison Japan's H-IIA vehicle is 53 m tall, 4 meters in diameter, Isp ~ 450 s, with an initial mass of 285 MT and delivers about 2 MT into GTO, figure 6. This vehicle that utilizes liquid hydrogen-oxygen for both stages plus some solid launch assist motors can be seen in detail at its website (http://www.jaxa.jp/projects/rockets/h2a/design_e.html). Thus, the metallic hydrogen propelled launch vehicles can deliver about 15 times the GTO payload for similar sized conventional launch vehicles.

Metallic hydrogen propelled vehicles clearly can revolutionize rocketry. The first step in this direction will be to prepare metallic hydrogen in small quantities in the laboratory and test to see if the assumptions used in this analysis are valid. If so, the next step would be to investigate means of economically scaling up production.

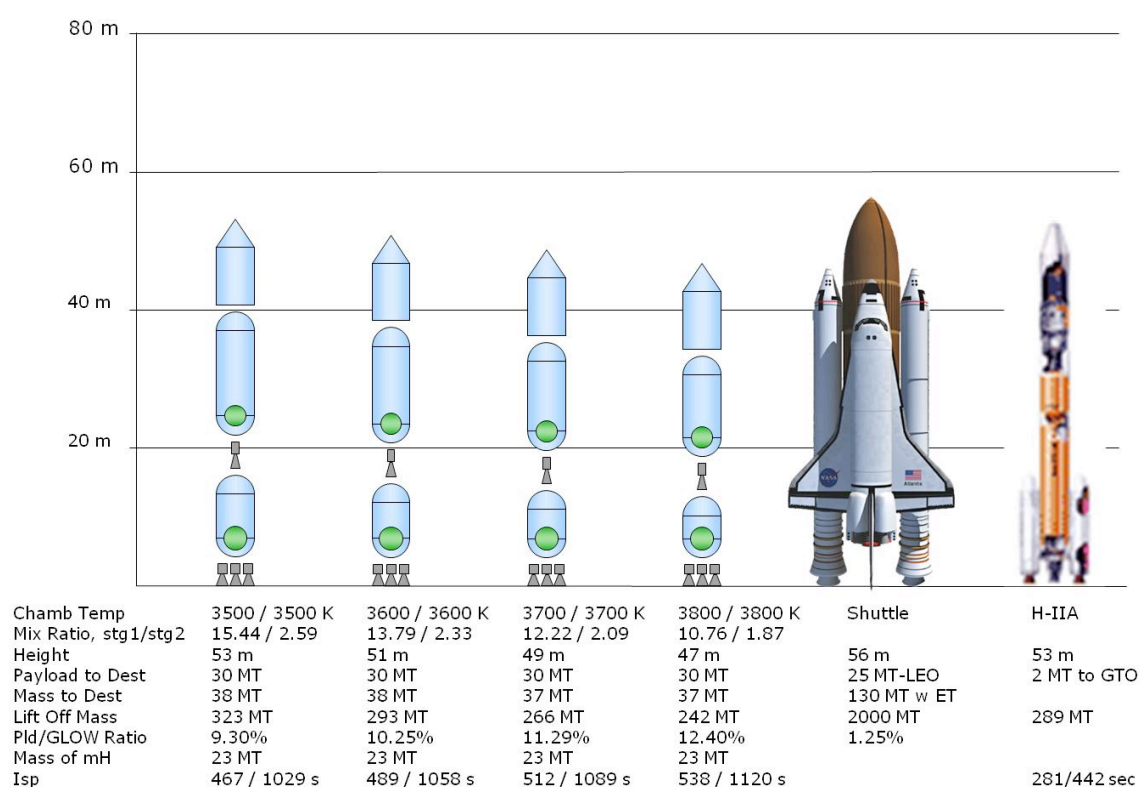


Figure 6. Metallic hydrogen propelled two stage launch vehicle concepts that deliver a 30 MT Payload into a Geosynchronous Transfer Orbit. The vehicles have various chamber temperatures determined by the dilution ratio. Stage 1 is diluted with water and stage 2 is diluted with liquid hydrogen.

Acknowledgments

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