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Upper Limits for Sublimation Losses from Hot Carbon Targets in Vacuum and in Gasses

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Introduction

One factor that needs to be considered in the selection and operation of hot carbon targets for the Muon Collider Project [1] are possible target life-time limitations caused by material removal due to sublimation. Carbon will be transferred from the hot target to cold surfaces, and buildup of carbon on walls and windows is another aspect that should be evaluated.

First rather straight forward estimates for sublimation in a vacuum are discussed, and then diffusion in a stationary He atmosphere is calculated. But a He atmosphere with large temperature gradients will not be stationary in the presence of gravity, as was correctly pointed out by several colleagues [2]. Crude but safe convection estimates are then presented. Finally the idea of possible chemical carbon re-deposition in atmospheres containing some hydrogen is briefly explored.

All our calculations and estimates are based on the equilibrium or saturation carbon sublimation vapor pressure. Values for temperatures from 1500 ^{o}C to 3000 ^{o}C were obtained from [3] and are shown plotted in fig, 1

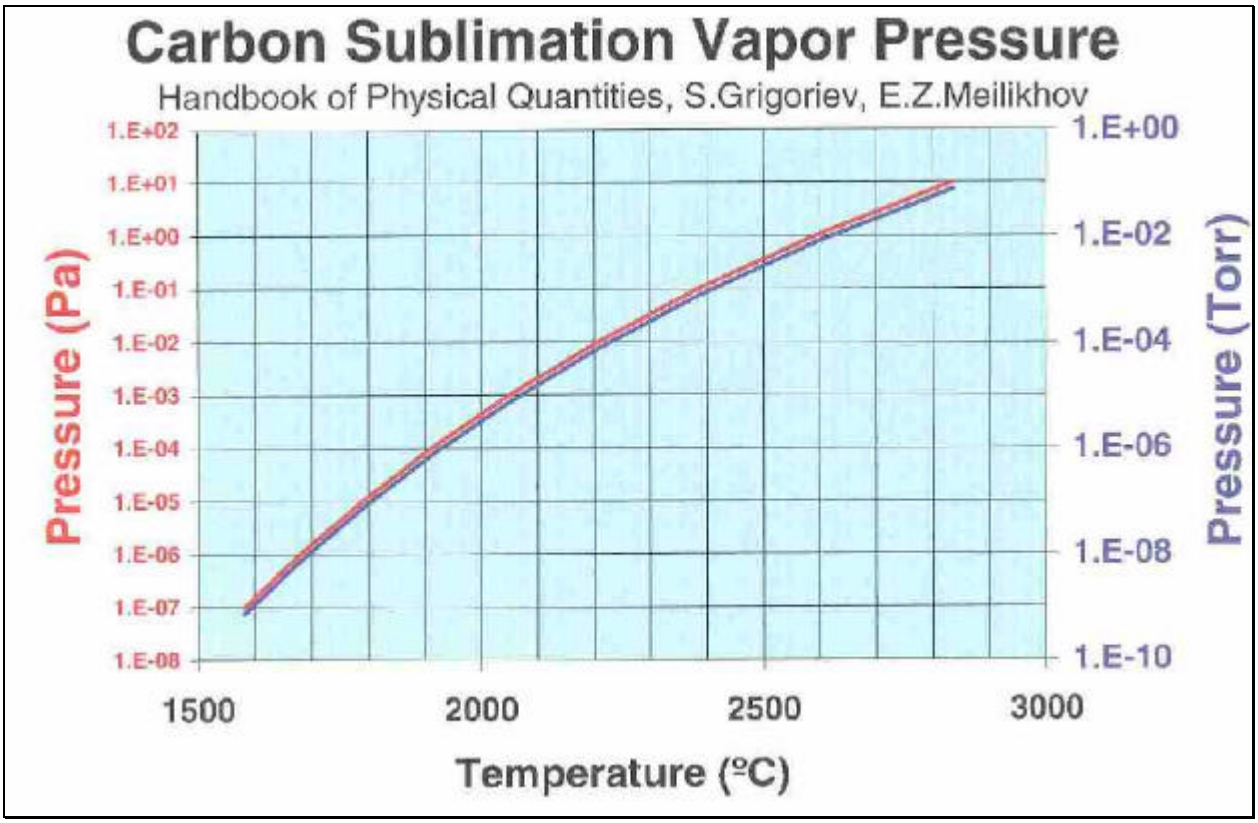


Fig. 1

Carbon sublimation vapor pressure as function of temperature. The lower curve corresponds to the right scale in Torr.

Sublimation in a vacuum

In order to estimate an upper limit for the rate of material loss due to sublimation of a hot cylindrical carbon rod at temperature T located in a cold, evacuated container, we make the following simplifying assumptions:

a) A thin boundary layer surrounding the target is at the equilibrium carbon sublimation pressure P_c for temperature T as indicated in fig. 1. The real, non equilibrium, pressure will of course be smaller, but its value is unknown, and will depend on the detailed characteristics of the surface.

b) All atoms within that boundary layer travel with the same speed, V, given by the mean thermal velocity obtained from a simplified kinetic theory of dilute gases [4]:

$V = \sqrt{8kT/mp}$ (1)

where k is the Boltzman constant, T is the temperature in ^oK, and m is the mass of the carbon atom.

c) No atoms leaving the boundary layer return to the hot surface. The validity of this assumption depends mainly on the sticking factor of the carbon atoms impinging on the cold surface since the mean free path for the temperatures and pressures of interest exceeds the size of the enclosure.

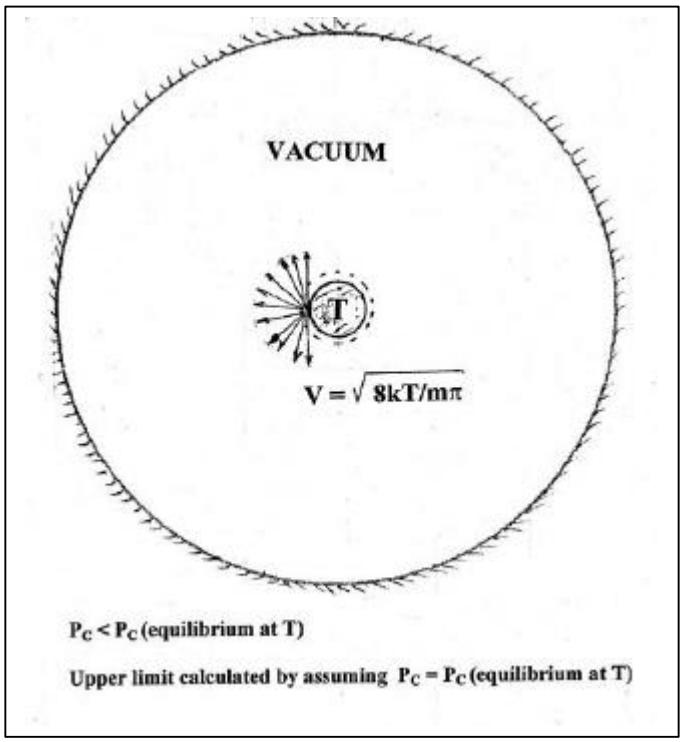


Fig. 2

The approximations made in a) and c) above will result in overestimates of the sublimation rate. Thus, we will obtain an upper sublimation limit for a typical temperature of interest e.g. 2200 ^oC. Before we do that, we must consider the fact that atoms will leave the boundary layer in all directions (fig.2). The flux out of the boundary layer will be determined by the mean velocity component $V_\perp$ perpendicular to that layer, which can be determined integrating the projections of the V-vectors over a half sphere. This yields a factor ½ to be applied to the velocity obtained from (1):

$V_\perp(2200^oC) = 1/2\sqrt{8kT/mp}$ (2)

$V_\perp(2200^oC) = 1/2\sqrt{8*1.38*10^{-23} JK^{-1} * 2473\ K / 12*1.67*10^{-27} Kg * p} = 1041$ m/s

The vapor density ρ in the boundary layer at 2200 ^oC will be:

$\rho = (0.01Pa / 1.013\times10^5 Pa) \times 12$ g/mol / $(22.4L/mol \times 2473^oK / 293^oK) = 6.27 \times 10^{-12}$ g/cm^3

where 0.01Pa is the equilibrium sublimation vapor pressure at 2200 ^oC obtained from fig.1 and 1.013×10^5Pa is the standard atmospheric pressure. ½ of these atoms will move towards the surface and the other ½ will move away with an average $V_\perp = 1.041 \times 10^5$ cm/s. The mass flux ϕ away from the surface is therefore:

$\phi = ½ \times 1.041 \times 10^5$ cm/s $\times$ 6.27×10^{-12} g/cm^3 = 3.26×10^{-7} g/cm^{2}s

For a graphite density of 2 g/cm^3, $(3.26 \times 10^{-7}$ g/cm^{2}s) / (2 g/ cm^3) = 1.63×10^{-7} cm/s is the velocity at which the radius of the rod would decrease. This would lead to a radius reduction of ~1 mm in 7 days. This time for a 1mm reduction is a lower limit due to the simplifying assumptions explained above.

Similar calculations were repeated for a number of rod temperatures between 1500 ^{o}C and 3000 ^{o}C and the results are plotted in fig.7 below, together with lower limits for loss times for sublimation in a helium atmosphere, with and without convection.

Diffusion estimates in stationary helium

As was mentioned in the introduction, "pure" diffusion (without convection) is not the dominant mechanism for mass transport in this case. However, this is the calculation that was carried out first. The results serve the purpose of confirming that the real effects are dominated by convection. The situation would be different in a micro-gravity environment where convection would become negligible. Also, since convection transport is much more difficult to estimate, we will only be able to obtain an upper limit for the convection-mediated sublimation rate. This diffusion estimate will be a good lower limit.

For this calculation a 1.5 cm diameter carbon rod at 2200 ^{o}C was placed in a 15 cm diameter cylindrical container at 27 ^{o}C, filled with helium at atmospheric pressure (fig. 3).

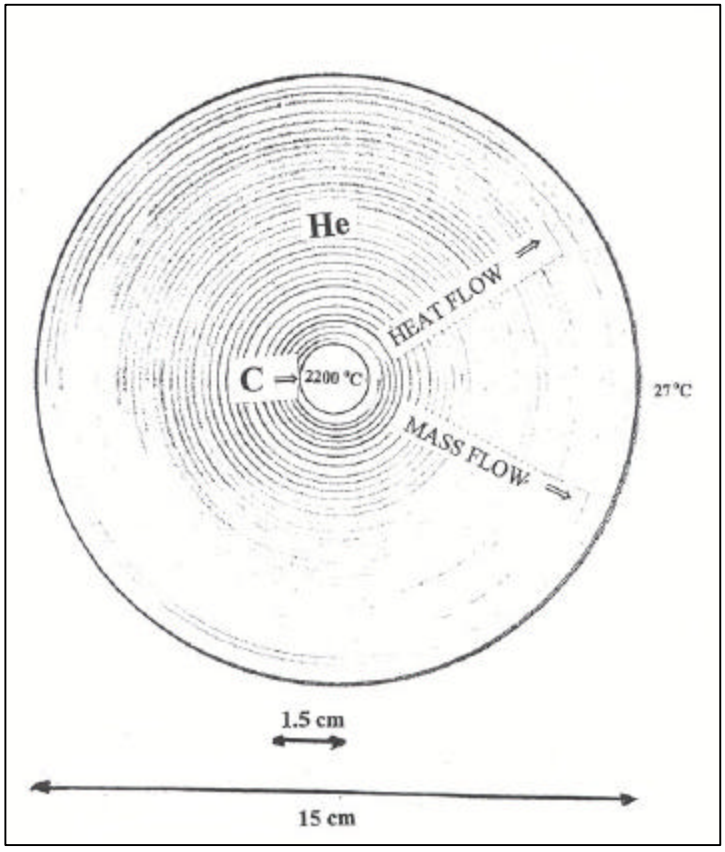


Fig. 3

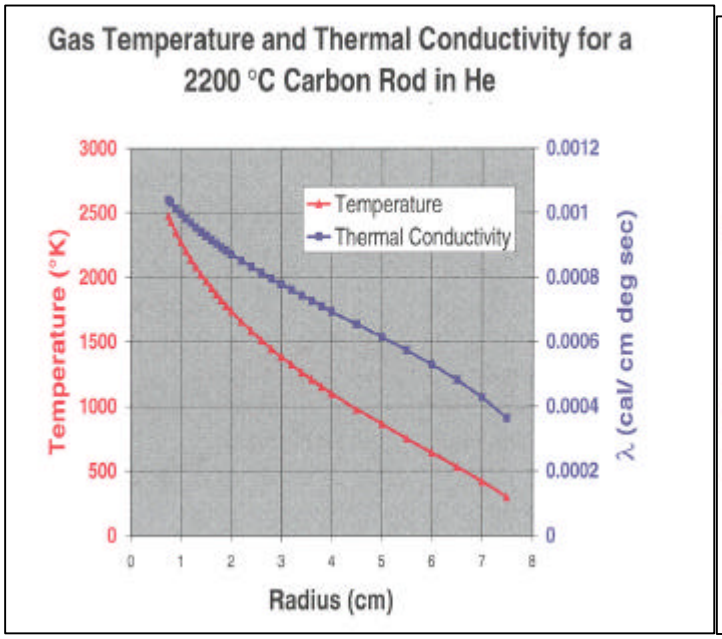
The first step is to calculate heat flow and radial temperature distribution. Since the carbon concentration in He will be extremely low (as can be seen form fig. 1), this can be done assuming pure He. We use a practical expression for the thermal conductivity λ [4, page 14], based on a simplified theory of dilute gases:

$\lambda = 1.9891 \times 10^{-4} (T/M)^{1/2} / \sigma^2$, cal /cm deg sec (3)

where

T = temperature in ^{o}K = 2473 ^{o}K
M = molecular weight = 4
σ = molecular diameter in Angström = 2.18A for He [4, page 15].

We divide the volume in cylindrical shells as indicted in fig.3. The innermost shell, is then assumed to be at the carbon rod temperature and its thermal conductivity is calculated using (3). Assuming an arbitrary initial heat flux, the temperature drop in the first shell yields the temperature for the second one. The new conductivity λ is computed , the heat flux is adjusted to take into account the new radius and the next temperature is obtained. This process is iterated until the outer surface is reached. At that point the temperature will in general be wrong due to the arbitrary initial heat flux. That flux is then adjusted until the correct outer temperature is obtain. This calculation was implemented using an Excel spreadsheet, and the iterations automated through its powerful "Solver" add-in.



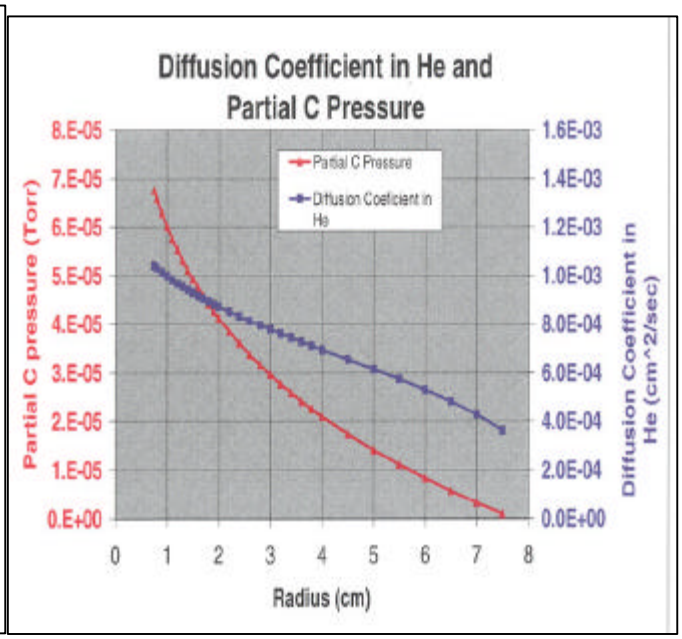


fig. 4 **fig. 5**

The results for the temperature profile and the conductivity as functions of the radius are shown in fig. 4. The heat flux at the rod surface was 1.008 cal/cm^{2}s in this case. The temperatures can now be used to calculate the mass diffusion coefficient of C in He at every point by using the formula based on a simple kinetic theory of dilute gases [4]:

$$D_{12} = 2.6280\times10^{-3}\frac{\sqrt{T^3(M_1+M_2)/2M_1M_2}}{p\,s_{12}^2}\ \text{, cm}^2\text{/sec} \qquad (4)$$

where p is the pressure in atmospheres and $\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2)$ is the average of the molecular diameters in Angström (M_1= 4, M_2=12, σ_1 = 2.18A, and σ_2 = 3A [4]) . Starting with the partial sublimation pressure at the layer closest to the rod, we get the pressure at the next layer by subtracting the product of an arbitrary mass flux times the diffusion constant D_{12}. We recalculate the flux and iterate this procedure, as we did before for the heat flow, until we reach the outer surface. Then we go back and automatically readjust the arbitrary mass flux by using Excel Solver, until we get a very small, non negative pressure at the cold surface. That mass flux is then the solution for the temperature T. For the present example (T = 2200 ^{0}C) we get a mass a flux of 1.46×10^{-11} g/cm^{2}s. Using 2 g/cm^3 for the density of graphite, we find that the surface of the solid recedes at 7.3×10^{-11} mm/s. That in turn means that it would take 1.585×10^5 days (434 years) for the radius of the rod to decrease by 1 mm if only transport by diffusion were significant. That time is then plotted as the 2200 ^{0}C point of the uppermost curve in fig. 7 below. The other points are calculated the same way.

It should be mentioned that there is another term called thermal diffusion which describes the mass transport due to temperature gradients, and we have only considered “normal” diffusion which is due to concentration gradients. That other term is thought to be small [4].

Crude convection limits

Mass transport in the presence of convection is a complicated phenomenon [5], difficult to estimate correctly, especially in a case like ours were large temperature differences lead to gas density variations of an order of magnitude when going from the hot surface of the rod to the room- temperature housing. The cooler gas will fall due to gravity, but there will be some buoyancy to slow it down.
We will exaggerate considerably if we adopt a maximum convection velocity V_2 equal to V_1 , the free-fall velocity for a distance equal to one radius (fig. 6). If we further assume that a boundary layer close to the rod contains carbon at a partial pressure equal to the equilibrium pressure given by fig. 1 and that the atoms in that layer move at a radial velocity $V_3 = V_2$ instead of $V_3 << V_2$ then we obtain a very rough, but also very safe upper limit for the rate of mass transport. The assumptions are briefly summarized at the bottom of Fig. 6. The result of these upper limit estimates are translated into minimum times for 1 mm reduction in radius and shown in fig. 7, below

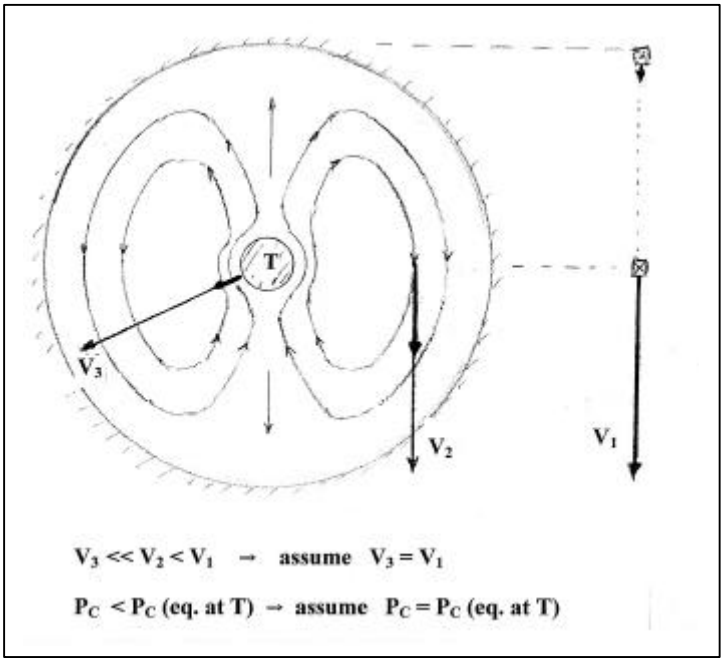


Fig. 6

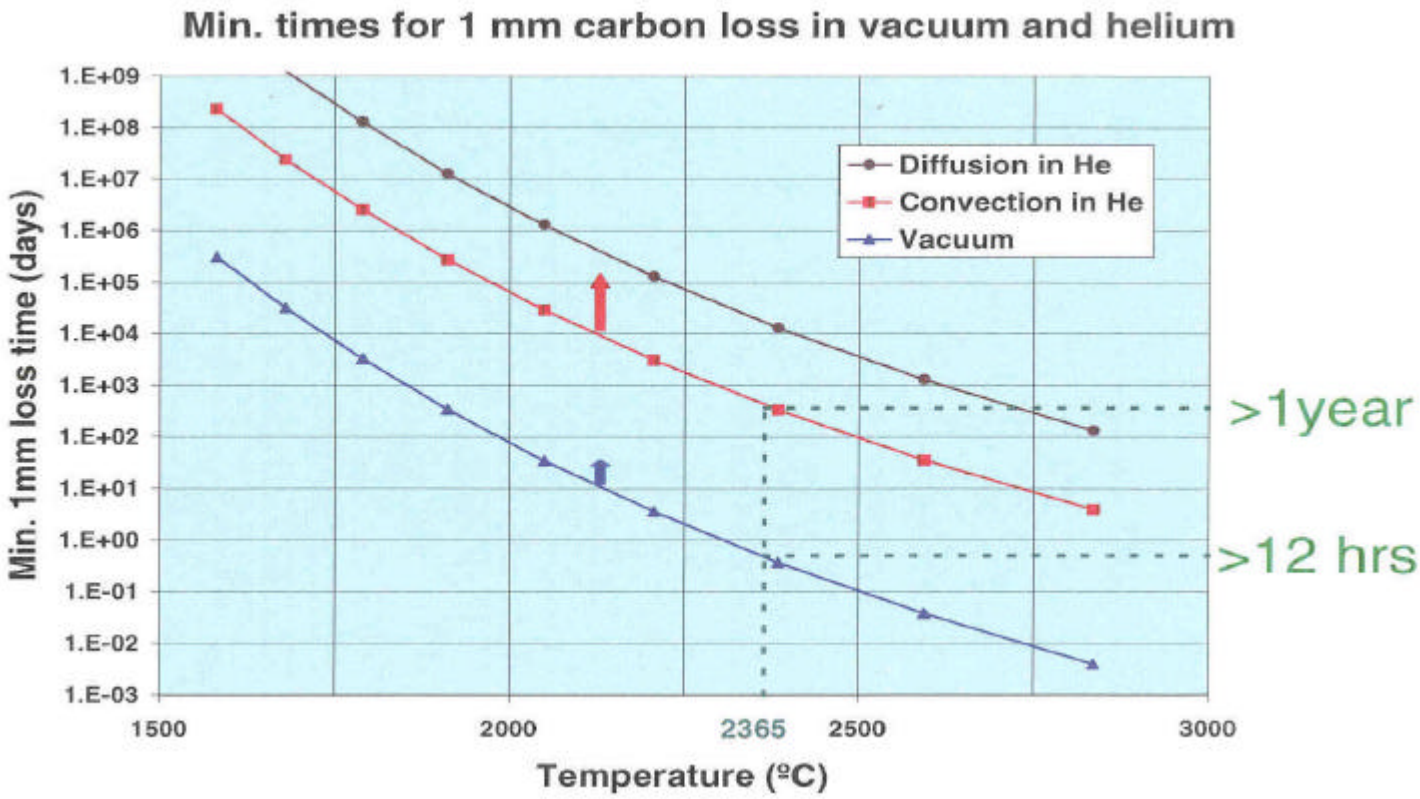


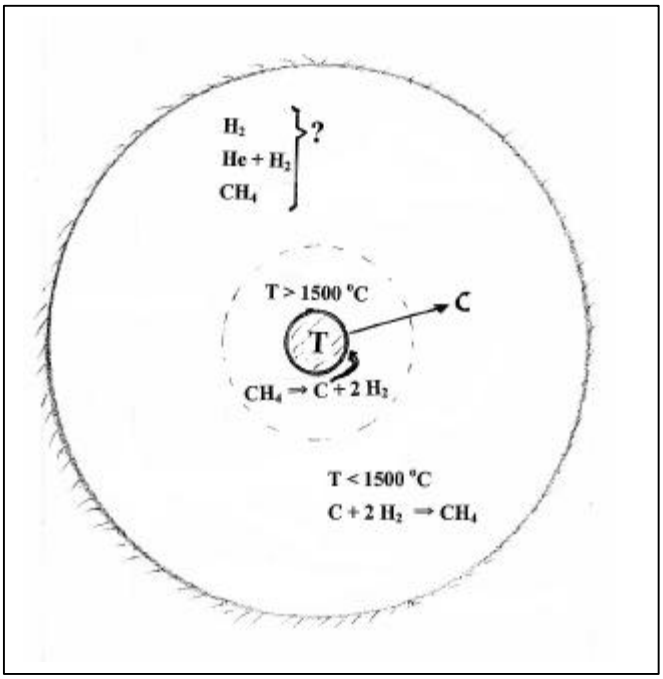
Fig. 7

The arrows indicate the fact that the curves are lower limits for the time it will take for 1 mm of material to be lost. For example, at 2365 ^{o}C that time will be longer than 12 hours in a vacuum and longer than one year in helium. Operation in He at 1 atmosphere may thus be satisfactory unless higher temperatures are generated. On the other hand it may be desirable to largely eliminate any sublimation losses and to avoid coating cold walls and windows with carbon. In the last section we discuss a simple approach to possibly re-depositing most carbon vapor on the hot surface.

Possible chemical re-deposition in the presence of hydrogen

The idea was to investigate if an approach similar to the one used in halogen lights could be found for carbon. "Conventional incandescent lamps lose filament material by evaporation, most of the material being deposited on the bulb wall. In a tungsten halogen bulb, halogen (iodine, bromine or fluorine) is added to the filling gas. If the correct temperatures are met, the discharged tungsten molecules from the filament will combine with the halogen molecules in the gas. The newly formed tungsten halogen molecules diffuse towards the filament, the tungsten being deposited back onto the filament, while the halogen is available for a further cycle. This regenerative cycle keeps the bulb clear for the entire life of the lamp." [6]

Quoting Helge Ravn [7] : "The halogen lamp principle which Peter Thieberger mentions [8] is derived from the van Arkel de Boer process also called Chemical Vapor Deposition used for producing samples of pure refractory elements. Ref. [9]. As a matter of fact it also works for Carbon and is widely used to coat other materials with graphite layer and a vast literature exist on the subject. The process depends on the chemical equilibrium of the reversible process: $2H_2+C = CH_4$, where mainly the temperature determines to which side of the equilibrium the process is shifted. If a graphite rod kept at temperatures above 1500^{o}C is exposed to a flow of methane as Helmut Haseroth [10] proposes. Carbon will be deposited and the excess hydrogen will be carried away. This is probably a viable way to replenish a graphite target."



The idea of Carbon deposition or re-deposition is illustrated in fig. 8 . While using CH_4 to deposit some carbon will work, the disadvantages are that the amount of CH_4 delivered would need to be controlled and that carbon deposits on cold surfaces wouldn't be avoided. If the indicated reactions with H_2 have adequate rates, then a H_2 or a He + H_2 atmosphere would be preferable. We would have a closed system without the need of adding gases, and carbon deposits on walls and windows would be avoided. Some measurements are planned to investigate the feasibility of this idea [11]

Fig. 8

The use of H_2 in a closed system like this, without the need for a connection to a gas tank, should not present any unusual safety problems. The accidental combustion of 1 mol of H_2 (which is roughly the amount that will be present) would generate 242 kJ, which should be compared to the ~2000 kJ [12] produced if the ~60g of hot Carbon burns. It is also possible that non flamable mixtures of H_2 and He may work, even though the maximum H_2 concentration is only 6.2% [13] .

Discussion and Conclusions

The crude approximations used here for obtaining conservative, convection-mediated mass transport limits can probably be refined. The phenomenon is however complex in that convection patterns are complicated and both, convection and diffusion are involved. Diffusion is predominant in boundary layers close to the hot and cold surfaces, and convection transport takes over in the bulk of the gas volume. Some simple measurements [11], would be useful to find real values instead of upper limits for sublimation losses.

The present upper limits for carbon sublimation loss-rates indicate that for a practical target life-time of one year, a temperature of 2365 ^{o}C is a safe value. To reduce losses further, to operate at higher temperatures and/or to have a cleaner system it may be sufficient to simply replace the He atmosphere with H_2 or with a H_2+He mixture.

References

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