Heart Cut for Higher Purity MOCVD Gas

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Many users of pure liquefied compressed gases such as arsine, ammonia or phosphine will only use the "heart cut" for the process. This means venting the first 10% of the cylinder using the next 80% and returning the remaining 10% (heel) of the cylinder which will concentrate the high boilers such as water.

Impurities in a liquefied gas cylinder such arsine are not homogenous. After filling in the cylinder and over time, impurities reach equilibrium in the vapor and liquid phases. This is based on their solubilities (Henry's Constant) or their liquid vapor pressures and other chemical properties. As a rule of thimb it is assumed that there is a factor of 10 difference between impurities in the liquid and vapor phases depending on the impurity. Numerous studies and articles have been written on this difference. It is not exactly a factor of ten and can differ based on impurity and other ambient conditions. This is not an exhaustive review and only select articles are referenced to support this.

The reason why distillation is effective is due to the many equilibrium stages in the column. A cylinder represents one equilibrium stage, in effect, a single plate distillation. As with all distillations, the composition of what remains inside the container changes over time. As the arsine is consumed by the user, the concentration of non condensible impurities increases. The more stages there are the more efficient the distillation. Analysis of a cylinder immediately after filling is not representative of what the customer sees when they use it.

Considerable research has been conducted on liquefied gas impurities primarily on arsine, ammonia, phosphine pure gases that are used for MOCVD processes as they are extremely sensitive to moisture and oxygen impurities. In addition, these processes require an extremely high gas flow rate in order to maintain deposition layer uniformity. This high flow rate has a direct impact on the impurities released from the liquefied gas.

Of all the references the most revealing is the work by Funke, et. al. [1] In this work they concluded that the ability to define a true equilibrium value between the liquid and gas phases (partition coefficient) for moisture in ammonia is influenced by many factors. This variability is shown in the following table where the ratio has considerable variation from 8 to 1 to 270 to 1 due to non equilibrium behavior in the cylinder.

Table I. Gas-Phase versus Liquid-Phase Moisture Concentration in Ammonia Cylinders*

Cylinder	Contents (kg of NH_3)	Gas Phase Moisture** (ppm)	Liquid Phase Moisture (ppm)	Liquid/Gas Moisture
1	13.62	~ 20	628 ± 8	31
2	0.61	~ 21	297 ± 5.3	14
3	22.72	~ 2.03	143 ± 1.9	72
4	15.45	~ 0.55	148 ± 1.6	270
5	15.45	~ 8.9	70.7 ± 0.8	8
6	22.72	~ 1.9	64.2 ± 0.8	34
7	6.81	< 0.1	2.9 ± 0.23	>30
8	22.72	n/a	0.2	n/a

*Flow rate: 0.8 slpm, cell pressure: ambient, cell temperature: 323.2 K.
**Minimum value reached during measurement, see text.

As noted in the following statement, measuring exact equilibrium values are a challenge.[2]

> Depending on the value of the partition co-efficient chosen, the gas phase moisture level can be inferred to be between ~ 0.4 ppb to ~ 12 ppb! However, the authors also reported a "quasi static" measurement of 227±15 for the partition coefficient, which is more likely to be the true partition coefficient at equilibrium.

In their testing they were able to demonstrate that the variability in liquid moisture concentration was low and stayed constant during the venting of the cylinder at a 2 slpm flow rate.

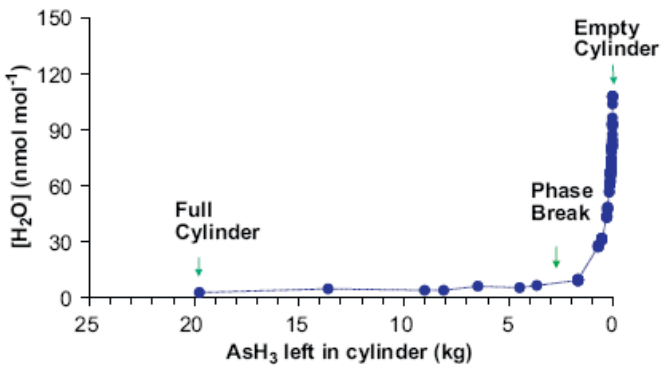
There are light and heavy impurities. Lights are the insoluble gases such as N_2, H_2, O_2, CO, CH_4, CO_2. These have a varying degree of solubility due to pressure, temperature and the concentration in the vapor space. They will be more concentrated in the vapor than the liquid and will decay as the gas is used. The heavies (H_2O) however will increase in concentration with use. This is why after filling most companies will vent a small amount of vapor to reduce the lights.

For purity critical semiconductor fabrication processes many researchers will use a heart cut of the gas cylinder. The first 10% of the gas is vented to reduce the lights. They then use it until there is a small liquid heel left and then switch to another cylinder. Vaporization of this heel would introduce a huge amount of water and other condensibles as shown in the following article from Matheson on moisture in arsine. [1]

> The full cylinder arsine (20 kg) contained water vapor concentration of ~4 nmol mol-1 and this concentration was maintained until the phase break ~2.7 kg. At this point no arsine liquid phase remained in the cylinder. The water vapor concentration remained approximately constant until about 1.8 kg of arsine remained. As the cylinder pressure dropped at the end of the depletion study to 137.9 kPa, the water vapor concentration increased to a maximum of 107 nmol mol-1. The profile of increasing water vapor (after the phase break point) follows the function below with a 0.95 correlation coefficient:

$C_{H2O.g} = 18.49^{-0.57}{}_{AsH3}$

To meet a 50 nmol mol_1 water vapor requirement in arsine gas, _0.18 kg arsine would need to be left in the cylinder, according to equation



Of importance to this discussion is a paper by Matheson which states[2]

A consequence of the solubility of moisture in the liquid phase of hydride gases is that moisture builds up in the cylinder as the more volatile matrix gas is removed and the less volatile moisture is left behind. Figure 4 shows the rise in moisture level that results from this concentration effect. The spike of moisture observed at the end of the measurement indicates the point at which the liquid phase of the cylinder is used up and the remaining moisture if flash-evaporated into the gas phase.

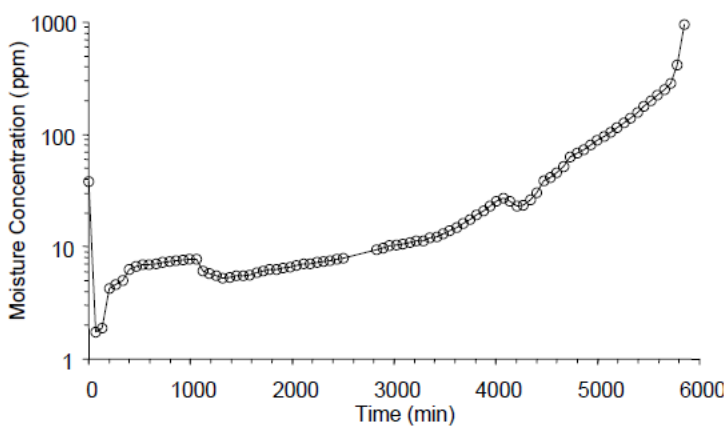


Figure 4. Moisture measured by FTIR in a standard cylinder of ammonia as the cylinder was emptied to dryness.

Note that this concentration is influenced by the vapor withdrawal flow rate.

The moisture in gas phase ammonia from the BSGU was measured at flow rates up to 1000 slpm. Figure I shows the gas phase moisture concentration in ammonia as a

function of flow rate. The data demonstrate that the free water concentration in the ammonia gas stream has a strong dependence on flow rate. The water concentration initially increases as the flow rate increases, reaches a maximum, and then declines as the flow rate continues to increase. This behavior was observed in two independent experiments. A detailed analysis of this phenomenon will be published elsewhere [5]. Briefly, it is a result of the combined effects of thermodynamics, fluid dynamics, and heat transfer within the BSGU. As the temperature of the liquid phase inside the BSGU decreases due to evaporative cooling, the temperature difference between the container wall and the liquid ammonia increases. The change in temperature profile causes the ammonia boiling mechanism to change within the BSGU, thus changing the moisture concentration in the gas phase with flow rate.

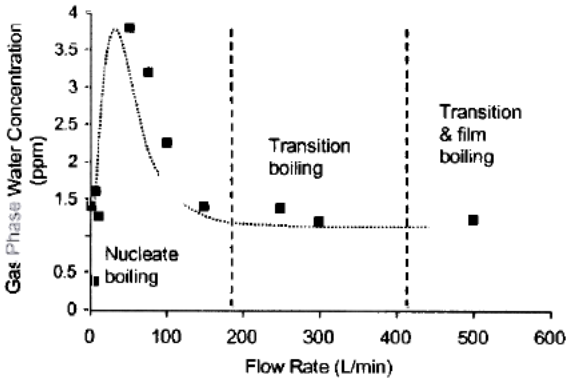


Figure 1. Change in the gas phase water concentration in ammonia as a function of flow rate from a gas phase delivery system.

Recent work by our group has focused on detection [2,3] and control [5] of trace impurities in the Group V hydride gases ammonia, arsine, and phosphine. Our results have begun to identify an important issue surrounding detection of impurities in condensed gases such as Group V hydrides. Because impurity measurements are traditionally made on the headspace gas of condensed gases, highly soluble impurities are often not accurately detected by conventional techniques. In effect, they are "iceberg" species, since the majority of their concentration lies unseen below the surface of the liquid.

One of our most significant discoveries has been the existence of trace moisture in the liquid phase of ammonia at concentrations up to 200 times that measured in the gas phase [2]. Figure 1 shows the partition of moisture between the gas and liquid phase of a cylinder of ammonia at near zero flow.

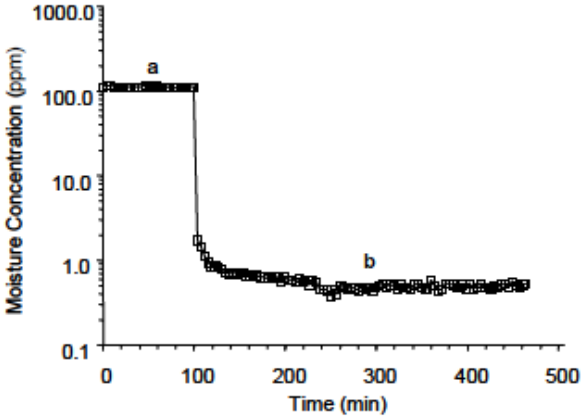


Figure 1. Moisture concentration in an ammonia cylinder sampled by FTIR from a) the liquid phase and b) the gas phase at near-zero flow.

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Liquid Heel

Estimate of when the cylinder completely vaporizes all the liquid (liquid dry) releasing the impurities concentrated in the liquid. To maintain ultra high purity, gas suppliers will weigh returned cylinders. If there is no liquid in the cylinder it must be filled with liquid, rolled and emptied liquid phase to recondition the cylinder.

Arsine

44 liter container
44 liters = 1.55385 ft^3
Density of AsH_3 at 70 F = 0.20 lbs/ ft^3
Vapor Pressure = 205 psig at 70 F
Liquid/ Vapor equilibrium at:
1.55385 ft^3 x 0.20 lbs/ft^3 = 0.31077 lbs at 1 atm
At 205 psig => 0.31077 x (219.7 / 14.7):
4.64 lbs left in container regardless of initial fill

Phosphine

44 liter container
44 liters = 1.55385 ft^3
Density of PH3 at 70 F = 0.0955 lbs/ ft^3
Vapor Pressure = 593 psig at 70 F
Liquid/ Vapor equilibrium at:
1.55385 ft^3 x 0.0955 lbs/ft^3 = 0.14839 lbs at 1 atm
At 593 psig => 0.14839 x (607.7 / 14.7):
6.13 lbs left in container regardless of initial fill

References:

1. Raynor, M., Clement, R., and Feng, J. "Characterization of high-purity arsine and gallium arsenide epilayers grown by MOCVD", J of Crystal Growth, 310, 2008, pp 4780-4785

2. Raynor, M., Sims, D., Funke, H., Watanabe, T., Fraenkel, D., Vininski, D., Owens, M. Torres, R., and Houlding V., “Detection and Control of Oxy-Impurities in Group V Hydride Gases and Gas Delivery Systems” Proceedings of CSMAX 2001, Boston, MA
3. Vininski,J., Yilcelen, B., Torres, R., and Houlding V. “Bulk Specialty Gas Systems For Ammonia Gas Phase Delivery V s. Liquid Phase Delivery”,

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