What we want to know about impurities in LAr

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What we want to know
Question #1

The most important (useful) question is:

What is the electron attachment to H_2O in LAr?

What we want to know
Questions #2

If the attachment coefficient is large, then it is important to understand how to minimize its presence in LAr. The important questions (all at 90K) are:

1. What is the solubility limit of H_2O in LAr?
2. What is the adsorption isotherm for H_2O on stainless steel?
3. Ditto for the adsorption/absorption of H_2O on/in plastics?
4. What is Henry's constant for H_2O in LAr?
5. What construction materials introduce the least (most) H_2O into the detector?

What we want to know
Questions #3

Independent of the relative importance of H_2O, we would like to determine:

1. Are there impurities other than O_2, H_2O, and N_2 in *commercial* LAr that limit the electron lifetime?
   a) Measure lifetime and O_2, H_2O, and N_2 concentrations, all simultaneously.
   b) Compute the lifetime from simultaneously measured concentrations and the known attachment coefficients.
   c) Compare a) and b); if they are significantly different, there are unknown impurities – find them.
2. Same questions for *purified* LAr with common construction materials immersed in it. Find any additional impurities from materials of construction that limit lifetime.

What we want to know
Questions #4

We believe, based on results shown in our purity paper, that a baffle might reduce the effective source of impurities into LAr.

1. Can we verify this ?
   a) What is the reduction in the true leak rate by the natural laminar flow region at the LAr surface?
   b) Can this reduction be maximized by adjusting operational parameters?
   c) Can an added baffle reduce this rate further?
2. What are the optimal parameters of such a baffle?

Can we measure the properties of H_2O in LAr
Questions #2

M&S needed

1. A purity monitor that operates at fields up to at least 1 kV/cm

1. What is the solubility limit of H_2O in LAr?
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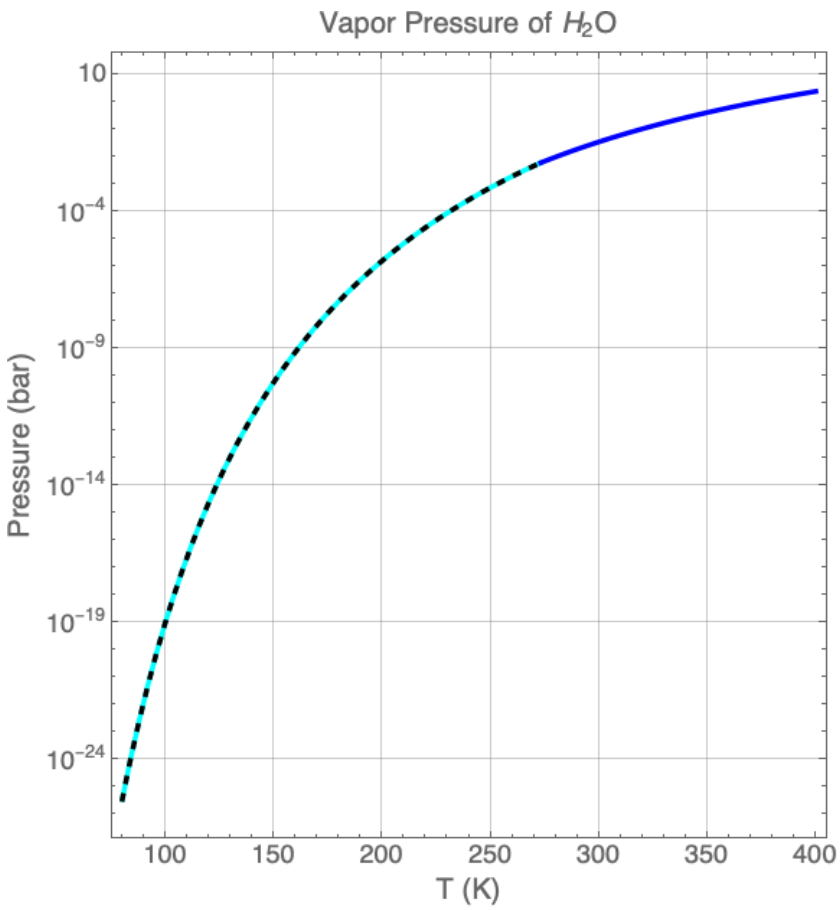
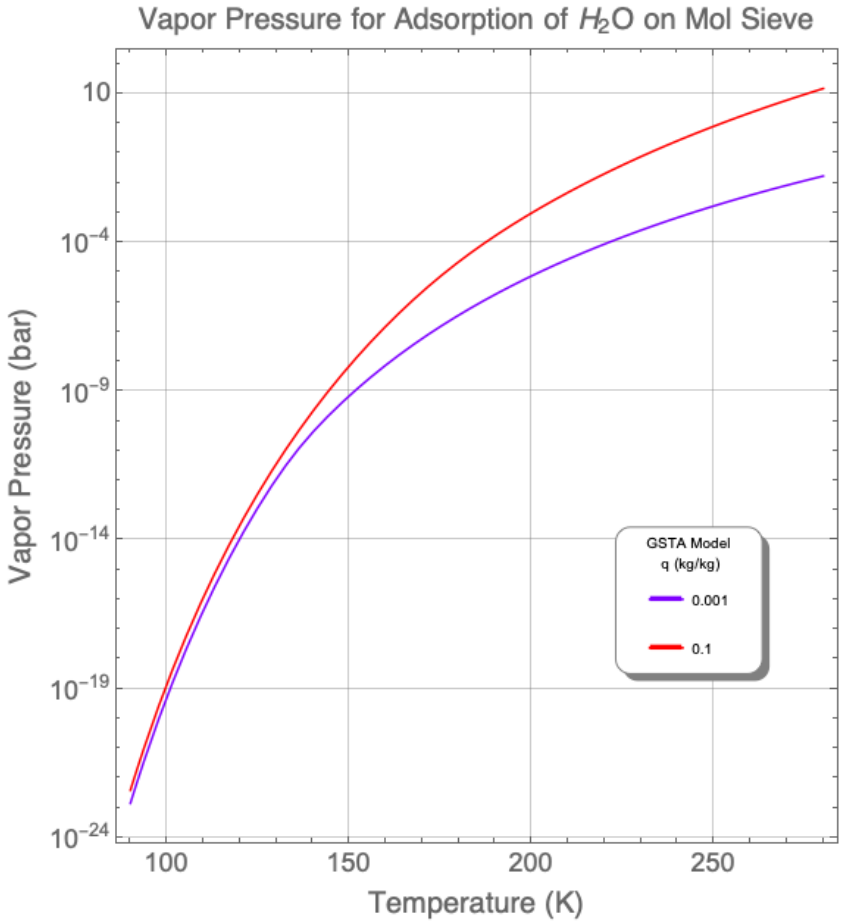
The Problem of Water in LAr

Vapor Pressure of H_2O

At 90K the vapor pressure of water ice is $1.39\ 10^{-22}$ bar, or 3.7 molecules/liter gas

The GSTA model fits for 13X imply a similar low vapor pressure at low temperatures.





1. W. Wagner, et al., J. Phys. Chem. Ref. Data 40 (2011) 043103.
2. N. Fray and B. Schmitt, Planetary and Space Science 57 (2009) 2053.

Desorption Rate Constants: Temperature Dependence

Water desorption by stainless steel and FR4

Water Desorption by FR4

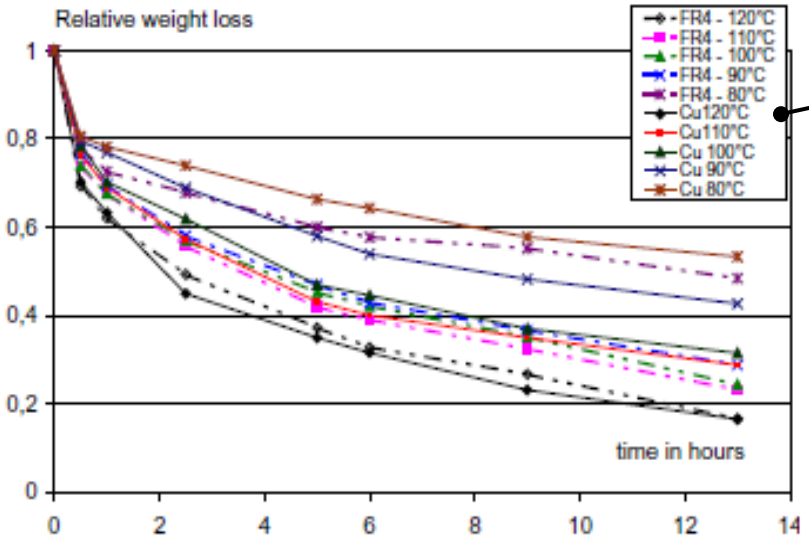
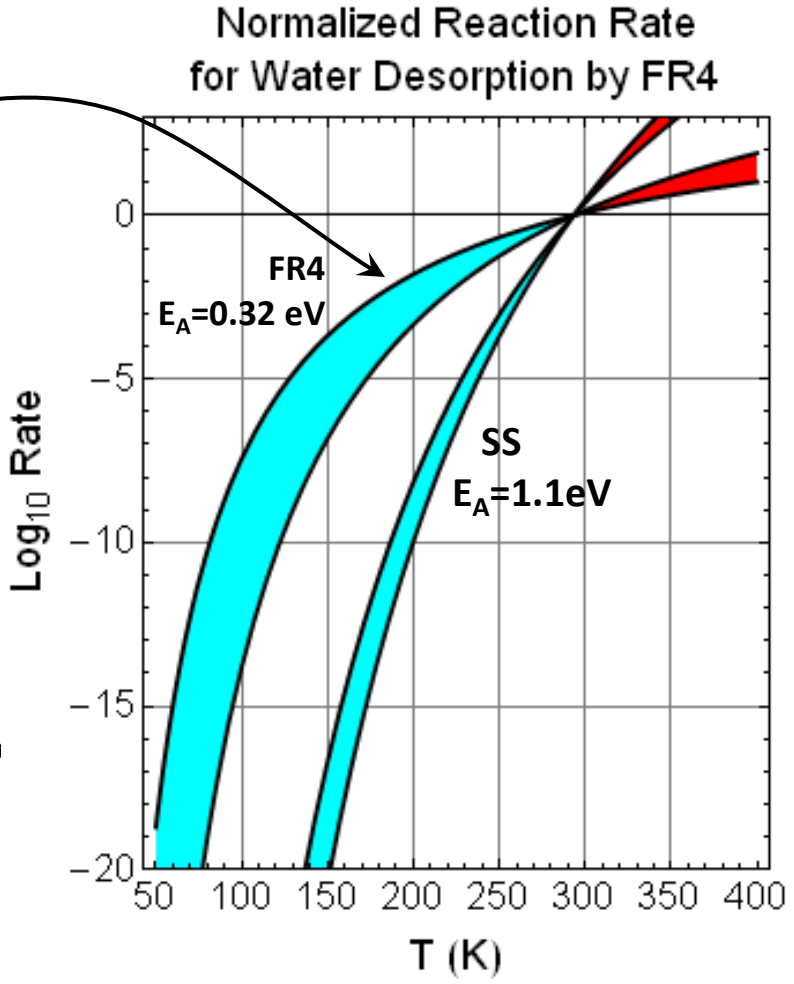


Fig. 3. Relative weight loss for 2 epoxy based PCBs at different temperatures.

$k_D(T) = Exp[-E_A/k(T-T_0)]$



FR4: *K. Weide-Zaage et al., Microelectronics Reliability 45 (2005) 1662*

SS: *J.H. Hendricks, Temperature Programmed Desorption Measurementsof the Binding Energy of Water to Stainless Steel Surfaces, AVS 54th Internationa Symposium (2007)*

Desorption rate depends strongly on temperature

1. Keep sources of impurities in liquid or cold gas
2. Maintain large flow in gas to dominate diffusion

The Problem of Water in LAr

So, to a first approximation, all water is in the LAr or on the surfaces in LAr, and the rate of release of water from surfaces is vanishingly small.

Leads to three questions:

1. What is Henry's coefficient for water in LAr?
2. What is the adsorption isotherm for water on SS at 90K?
3. What is the adsorption rate for water on SS?

Henry's Coefficient for H_2O in LAr

It is probably small, contrary to popular opinion. If so, gas purification may not be very effective.
Can we verify this?

Henry's Coefficient for H_2O in LAr

Here is what we know about Henry's coefficient of H_2O in LAr:

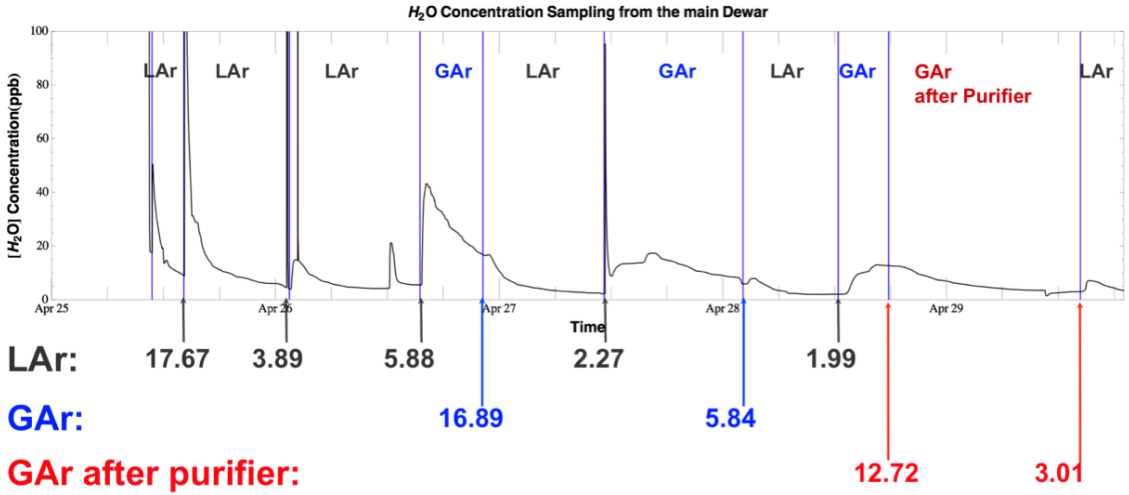
1. NIST program REFPROP v8 [1] gives $3x10^{-9}$ at 90 K , and REFPROP v10 [2] gives $4.1x10^{-3}$ at 90 K.
2. Andrews, et al. [3] report that the concentration of water in GAr is 500 times the concentration in LAr without any explanation; however this is certainty not measured in equilibrium conditions, and, because of the "Baffle Effect", is probably much larger than Henry's coefficient.
3. We have made measurements suggesting a value of Henry's coefficient in LAr between 0.04 and 4, although these are not equilibrium measurements either. In the two next slides we briefly explain our measurements.

1. https://www.nist.gov/srd/refprop
2. Same source as above, but v10 uses new mixing parameters from J. Gernert and R. Span, J. Chem. Thermodyn., 93 (2016) 274: DOI:10.1016/j.jct.2015.05.015
3. R. Andrews, *et al*., NIM A608 (2009) 251.

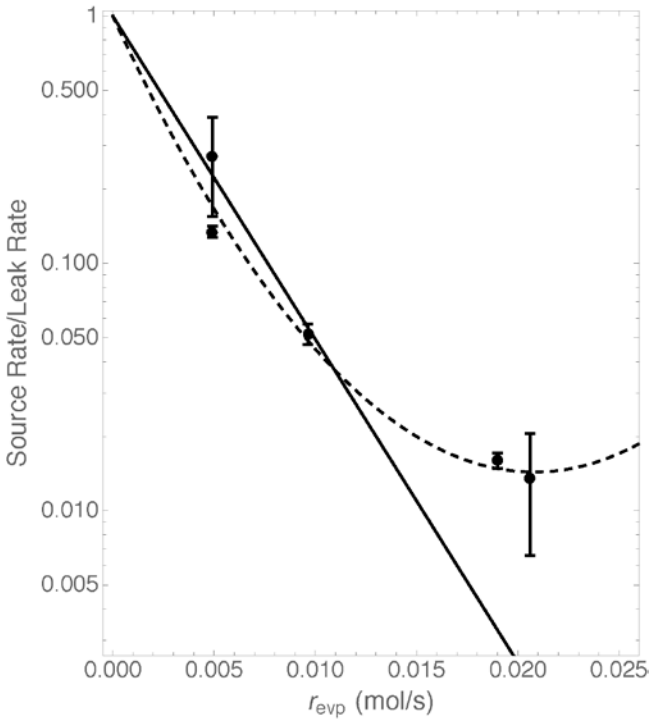
Henry's Coefficient for Water in LAr

Method 1: By direct measurement of water in both GAr and LAr.

By alternately measuring the water concentration in the flow of gas from a tube terminating in the liquid, and from a tube terminating in the gas a few inches above the liquid, we obtain a value of H_{xx}=3.5±1.9. However, this is not an equilibrium measurement.



However, because the "Baffle Effect" (aka diffusion against flow) causes the gas above the liquid to increase with height above the surface, the true concentration in the gas at the surface is probably 10 to 100 times smaller that what we measure. **This would imply 0.4 > H_{xx} > 0.04.**

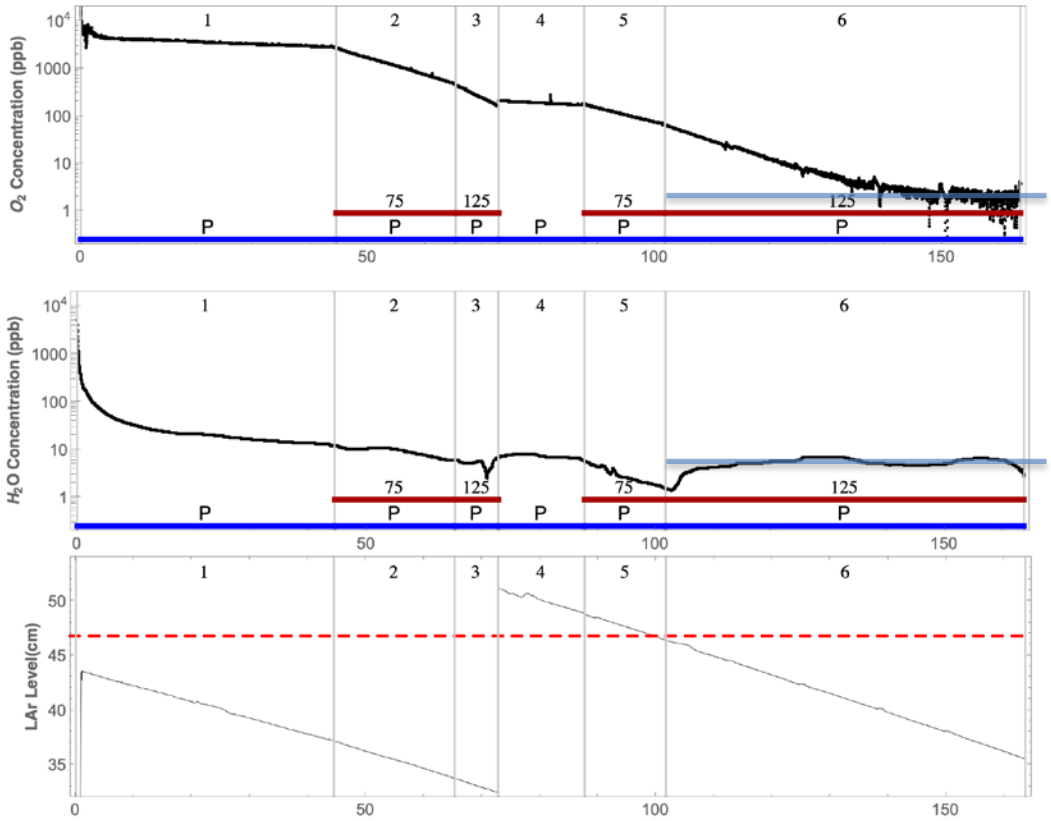


Henry's Coefficient for Water in LAr

Method 2: Simultaneous observation of the steady state concentrations of O_2 and H_2O in LAr with purification, using Eq 2.33 of our purity paper (arXiv:2009.10906)

$$c_{i,l}^{ss} = \frac{r_{lek,i}}{H_{xx,i}\ r_{evp}\ \varepsilon_{P,i}} \text{ if } r_{sam} \to 0$$

$$\text{assume } \varepsilon_{P,O_2} = \varepsilon_{P,H_2O} > 0$$



2ppb

5ppb

The ratio of H_2O to O_2 in air at 50% RH is 0.056. The measured ratio of steady state concentrations is 5/2=2.5. Henry's coefficient for O_2 is 0.91.

This implies that for H_2O $H_{xx} = 0.02$

Note that, by comparing the rate of change of concentrations for H_2O to O_2, it is clear that adsorption dominates evaporation.

Henry's Coefficient for H_2O in LAr from the Theory of Regular Solutions

See J.H. Hildebrand and R.L. Scott, Regular Solutions, Prentice Hall, NJ (1962)

Henry's Coefficient for Impurities in LAr

from Dalton's and Raoult's Laws

Dalton's Law is

$$P_{Total} = \sum_{i=1}^{n} P_i$$

Raoult's Law is

$$P_i = x_i P_{Vap,i}$$

Therefore, for the gas phase of a two component (Z in LAr)

$$P_Z = x_Z P_{Vap,Z}$$

$$P_{Ar} = (1 - x_Z) P_{Vap,Ar}$$

x is mole fraction in liquid
y is mole fraction in gas
$x_1 = 1 - x_2$

And Henry's coefficient is

$$H_{xx} = \lim_{x \to 0} \frac{y}{x}$$

$$y = \frac{P_Z}{P_{Total}} = \frac{x_Z P_{Vap,Z}}{x_Z P_{Vap,Z} + (1 - x_Z) P_{Vap,Ar}}$$

$$H_{xx} = \lim_{x_Z \to 0} \frac{P_{Vap,Z}}{x_Z P_{Vap,Z} + (1 - x_Z) P_{Vap,Ar}} = \frac{P_{Vap,Z}}{P_{Vap,Ar}}$$

This is the result for an "**Ideal Solution**", in which both components in both phases behave as ideal gases, and there is no heat of mixing (We ignore the fact that somehow these ideal gases condense).

Henry's Coefficient for Impurities in LAr

for "Ideal Solutions"

Henry's coefficient for Ideal Solution is $H_{xx} = \frac{P_{Vap,Z}}{P_{Vap,Ar}}$

Henry's coefficients for Ideal Solutions

Species	H_{xx} Ideal	H_{xx} Meas	Ideal/Meas
Ar	1.	1	1.
N2	2.7	3.5	0.77
O2	0.74	0.9	0.83
CO	1.8	2.8	0.64
CH4	0.081	0.12	0.67
C2H6	8.2×10^{-6}	0.000077	0.11
C3H8	$3. \times 10^{-9}$	$7. \times 10^{-8}$	0.043
CF4	0.00076	0.0012	0.63

"Ideal Solution" model is not too bad!

Henry's Coefficient for H_2O in LAr

for an "Ideal Solution"

Henry's coefficient for H_2O in LAr is $H_{xx} = \frac{P_{Vap,H_2O}}{P_{Vap,Ar}}$

For the vapor pressure of ice, see Rainer Feistel, and Wolfgang Wagner, *Sublimation pressure and sublimation enthalpy of H_2O ice **Ih** between 0 and 273.16 K*, Geochimica et Cosmochimica Acta **71** (2007) 36.

The range of the measured data set is stated to be 273.15K $\geq$ T $\geq$ 130K, corresponding to pressures ranging from 6.11×10^{-3} bar to 4.78×10^{-13} bar. There are 216 data points in the set. Below 130K the sublimation pressure is constrained by thermodynamic relations.

From their Table 4 of this reference, the vapor pressure of ice at 90K is 1.39×10^{-22} bar. The vapor pressure of LAr at 90K is 1.33 bar.
This gives Hxx = 1.04×10^{-22} at 90K – could it really be this small?

- If not, there must be a large chemical interaction between water and LAr.
- This is actually the case for water vapor in air – absolute humidity is greater than the vapor pressure of water divided by atmospheric pressure.

Henry's Coefficient for a "***Regular* Solution"**: chemical interaction

A "Regular Solution" model improves the "Ideal Solution" model by allowing heat of mixing, but requires that the entropy change be that of the ideal solution, namely $-R\, x_i\, ln(x_i)$ per mole.

Then, Henry's coefficient for impurity 1 in solvent 2 is

$$H_{xx} = \frac{P_{Vap,1}}{P_{Vap,2}} Exp\left(\frac{v_{M,1}}{RT}\left(c_{11} + c_{22} + 2(1-L_{12})\sqrt{c_{11}c_{22}} \right) \right)$$

where

$$c_{ii} = -\Delta H_{Vap} \Big/ v_{M,i}$$ and $v_{M,i} =$ molar volume of i

c_{ii} is the "cohesive energy" of component i.

$c_{i2} = (1\text{-}L_{12})\,(c_{11}\, c_{22})^{1/2}$ defines L_{12}, a parameter that is near zero when solute and solvent are similar.

J.H. Hildebrand and R.L. Scott, Regular Solutions, Prentice Hall, NJ (1962)

J.M. Prausnitz, Molecular Thermodynamics of Fluid-Phase Equilibria, Prentice-Hall, Englewood Cliffs NJ (1969) 263 *et seq*.

E.R. Bazua and J.M. Prausnitz, *Vapor - liquid equilibria for cryogenic mixtures*, Cryogenics 11 (1971) 114.

Henry's Coefficient for "Regular Solutions"

Henry's coefficient for a "Regular Solution" is

$$H_{xx} = \frac{P_{Vap,1}}{P_{Vap,2}} Exp\left(\frac{v_{M,1}}{RT}\left(c_{11} + c_{22} + 2(1 - L_{12})\sqrt{c_{11}c_{22}} \right) \right)$$

Henry's coefficients for Regular Solutions

Species	H_{xx} Reg	H_{xx} Meas	L_{12}	Reg/Meas
Ar	1.	1	0	1.
N2	3.5	3.5	−0.014	0.998
O2	0.91	0.9	0.011	1.01
CO	2.6	2.8	0.005	0.92
CH4	0.12	0.12	0.018	0.991
C2H6	0.000077	0.000077	0.012	1.
C3H8	7.1×10^{-8}	$7. \times 10^{-8}$	0	1.01
CF4	0.0012	0.0012	0	0.96
H2O	1.9×10^{-8}	1.	0	1.9×10^{-8}
H2O	1.	1.	0.49	1.

} ?

Excellent agreement with measurements!

Henry's coefficients and Solubilities in LAr

Solute	H_{xx}	x_2 Max	Reference
N_2 (*g*)	3.5	1	1, 2, 8, 12
O_2 (*l*)	0.9	1	1, 8, 12, 24, 25, 26, 27, 28
He (*g*)	4150	?	10
Ne (*g*)	955	0.9	10, 11, 13, 14, 15
Kr (*s*)	2.2	0.35	1
Xe (*s*)	$<10^{-5}$	0.05	16
H_2 (*g*)	780	0.25	5, 9
D_2 (*g*)	610	?	5
CO (*g*)	2.8	1	1, 12
CO_2 (*s*)	?	2.6×10^{-6}	3, 4, 6
CH_4 (*s*)	0.12	?	1, 2, 7
CF_4 (*s*)	0.0012	?	1
Ethane (*s*)	0.000077	?	1
Propane (*l*)	$7.\times10^{-8}$	?	1
1,3–Butadiene (*s*)	?	$9.\times10^{-7}$	3
Pentane (*s*)	?	9.4×10^{-6}	3, 18
2–Methylbutane (*s*)	?	0.000014	17, 18
Neopentane (*s*)	?	0.00082	3
1–Pentene (*s*)	?	$7.\times10^{-7}$	17
Isoprene (*s*)	?	2.4×10^{-6}	23
Cyclopentane (*s*)	?	9.3×10^{-8}	3, 18, 22
Cyclopentene (*s*)	?	7.1×10^{-6}	21
Hexane (*s*)	?	1.4×10^{-7}	19
2–Methylpentane (*s*)	?	2.3×10^{-7}	20
1–Hexene (*s*)	?	6.7×10^{-7}	20
1–Hexyne (*s*)	?	1.5×10^{-7}	21
Cyclohexane (*s*)	?	1.6×10^{-7}	19
2,3–Dimethylbutane (*s*)	?	$7.\times10^{-7}$	3, 22
H_2O (*s*)	2	$3.\times10^{-7}$	4, 26, 28
N_2O (*s*)	?	0.000074	4
Dimethyl ether (*s*)	?	0.000013	4
Diethyl ether (*s*)	?	4.5×10^{-6}	4
Di–n–propyl ether (*s*)	?	3.7×10^{-6}	4
Di–isopropyl ether (*s*)	?	$2.\times10^{-7}$	4

We need to determine both the Henry coefficient for water in LAr and the maximum solubility of water in LAr and GAr

NIST program REFPROP gives
$H_{xx} = 3.4\text{x}10^{-9}$ for H_2O in LAr at 90K

"The solubilities of H_2O, H_2S, CH_3OH and C_2H_5OH in LN_2 (115 K), LO_2 (135 K) and LAr (128 K) were therefore found to be below the limit of detection using IR spectroscopy, i.e. considerably less than 10^{-8} mole fraction."

A.J. Rest, R.G. Scurlock and M.F. Wu, *The Solubilities of Nitrous Oxide, Carbon Dioxide, Aliphatic Ethers and Alcohols, and Water in Cryogenic Liquids*, Chemical Engineering Journal, 43 (1990).

Consequences for electron attachment:

[no one but us has measured H_2O in LAr]

An Observation of Water Dissolving in GAr and in LAr

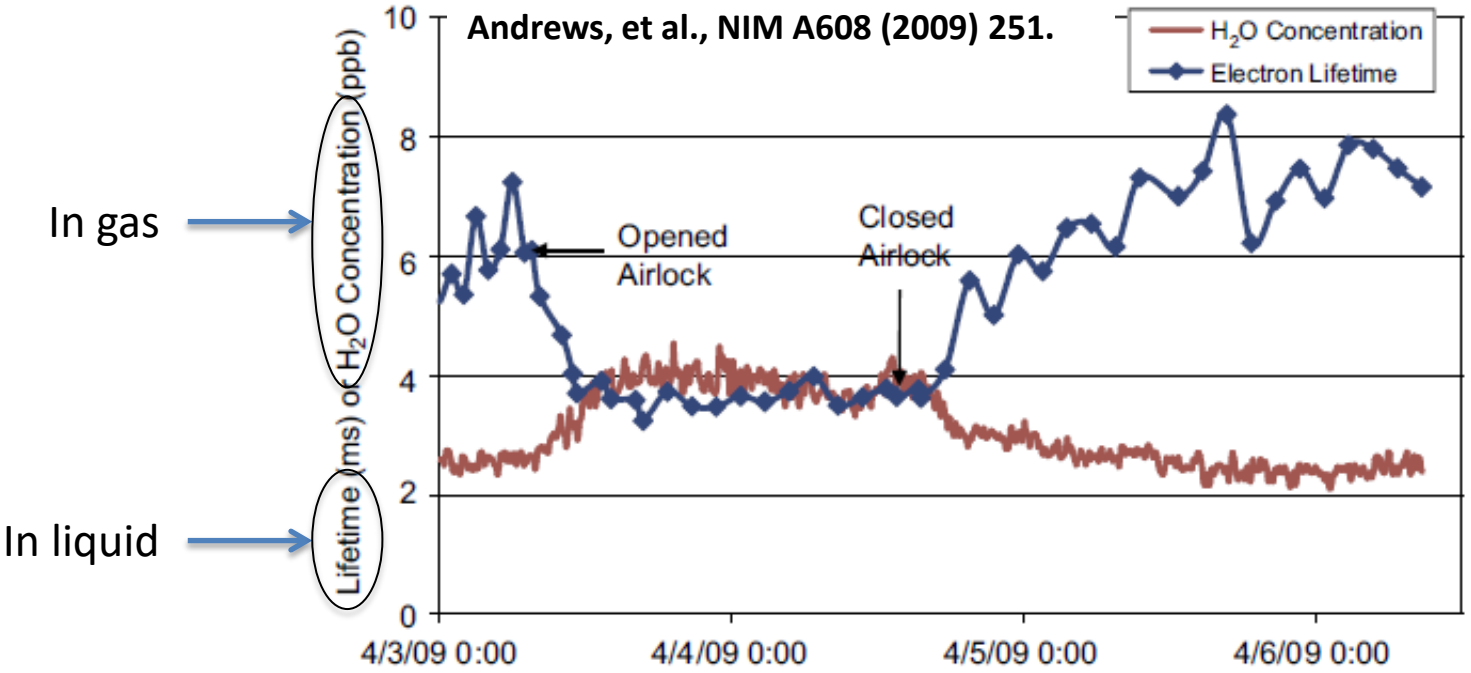
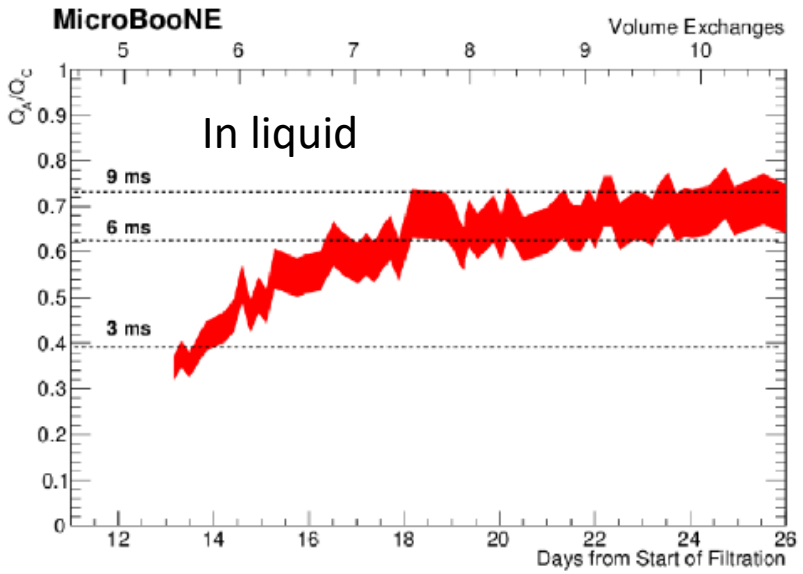
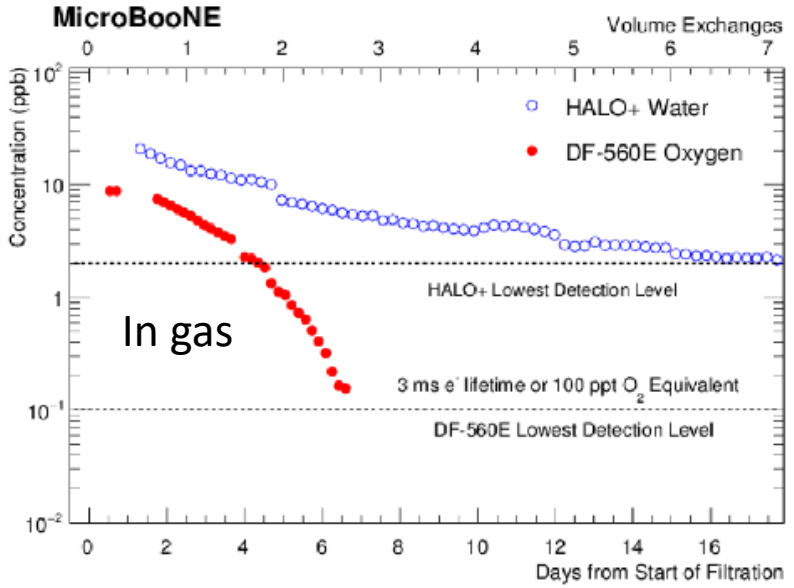


Fig. 7. Effect of connecting cryostat and airlock volumes. The cryostat was connected to the airlock by opening the gate valve that typically separates the two. Prior to opening, the airlock was under vacuum. The increase in water concentration is attributed to the additional warm metal surface area in contact with the argon vapor. The relationship between water concentration and drift lifetime is similar to the relationship observed during materials testing (e.g. Fig. 8). This test was performed with 15 in. LAr in the cryostat.

Estimate of Attachment Rate for H_2O

B. Carls and M. Zuckerbrot, MicroBooNE docDB 4823, 10/27/2015.





Our value of $H_{xx} = 2$:

Estimate $k_A(H_2O) = (1.37 \pm 0.11) \times 10^{11}\ s^{-1}$ from the data above

Estimate $k_A(H_2O) = (1.23 \pm 0.16) \times 10^{11}\ s^{-1}$ from the data of Andrews (slide 8)

NIST REFPROP value of $H_{xx} = 3.4 \times 10^{-9}$:

Estimate $k_A(H_2O) = 230\ s^{-1}$ from the data above

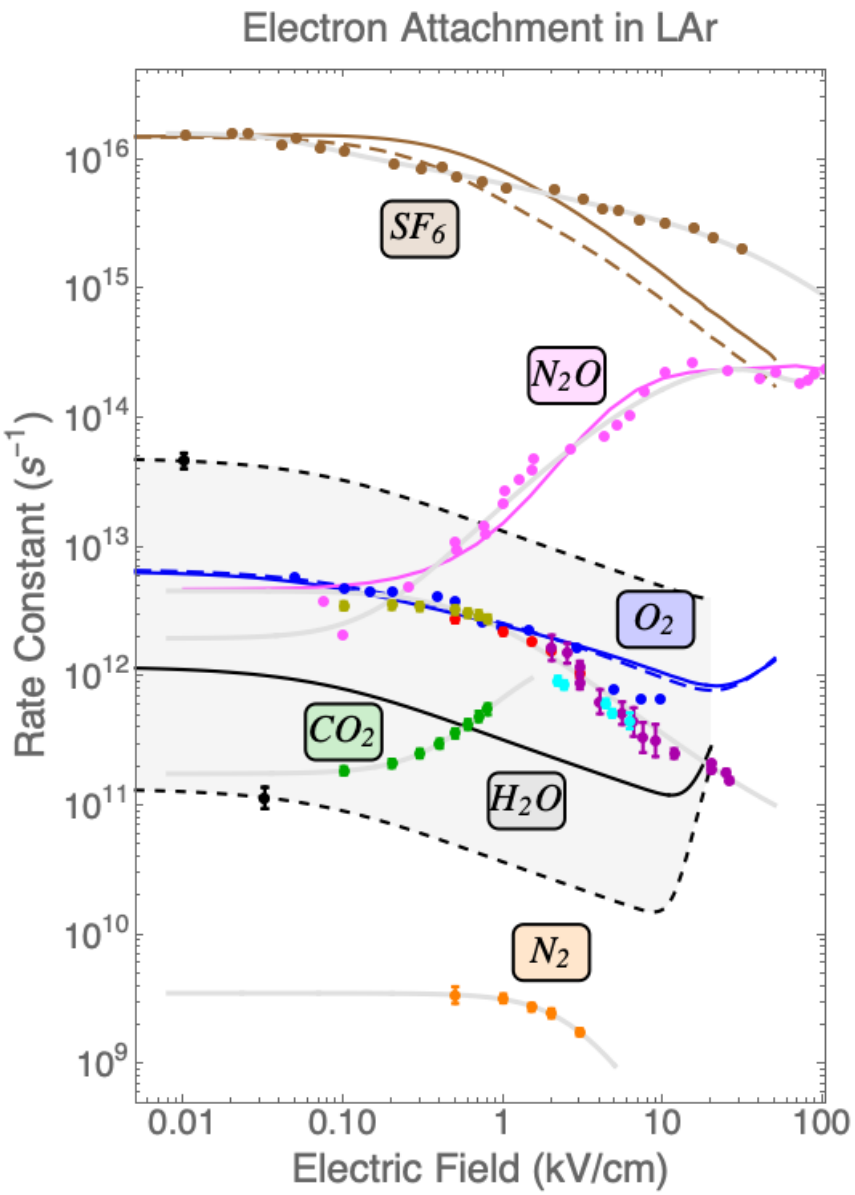
Estimate $k_A(H_2O) = 210\ s^{-1}$ from the data of Andrews (slide 8)

Andrews, et al. value of $H_{xx} = 500$:

Estimate $k_A(H_2O) = 3.4 \times 10^{13}\ s^{-1}$ from the data above

Estimate $k_A(H_2O) = 3.1 \times 10^{13}\ s^{-1}$ from the data of Andrews (slide 8)

Calculated Attachment Rates



1. The light gray curves are the best fit to a Pade function constrained to $dk_A/dE=0$ @ E=0.
2. The solid & dashed curves are calculated from cross sections with the modified Maxwell energy distribution described above.
3. For H_2O three calculations are shown, each using a different magnitude of the radiative attachment cross section, but the same dissociative attachment cross section.
   a) The solid black line matches the low field attachment implied by the measured electron affinity (see slide 25)
   b) The two dashed black lines match the values implied by our analysis of the data of Carls [1] (low value) and the data of Andrews [2] (high value), shown as black points.

1. B. Carls and M. Zuckerbrot, μBooNE DocDB 4823.
2. R. Andrews, et al., NIM A608 (2009) 251.

Cross Sections, Electron Affinity, and Dissociation Energies

Species	e_A(eV)	$e_{Diss,Mol}$(eV)
SF_5	3.66	
Cl	3.613	n/a
F	3.401	n/a
SF_3	3.07	
F_2	3.01	1.60
Cl_2	2.38	2.48
SF_4	2.35	
NO_2	2.273	
O_3	2.103	
OH	1.828	4.39
O	1.461	n/a
SO	1.125	5.36
SO_2	1.107	5.67
→ SF_6	1.07	3.38
H	0.7542	n/a
→ O_2	0.451	5.12
NH	0.22	3.51
→ N_2O	0.22	1.71
NO	0.026	7.59
→ H_2O	0	5.12
NH_2	0	4.23
NH_3	0	4.66
N	−0.07	n/a
→ CO_2	−0.6	5.45
→ N_2	−1.6	9.76
CO	−1.8	11.10
H_2	−2.5	4.48

Electron affinity is the energy of this reaction:

$$e^- + X \rightarrow X^- + \Delta E_{EA}$$

Dissociation energy is the energy of this reaction:

$$XY + \Delta E_{Dissoc} \rightarrow X + Y$$

For dissociative attachment

$$e^- + XY \rightarrow X^- + Y + \Delta E_{Dissoc}$$

The threshold energy is

$$\Delta E_{Dissoc}(XY) - \Delta E_{EA}(X)$$

While every atom and molecule has an IP, they need not have an EA. There is a large class of anions which are not bound species. Many common molecules such as N_2, H_2O, and C_6H_6 do not form stable anions. In the gas phase H_2O^- decays to H_2O plus a free electron … the carbon dioxide anion is meta-stable for roughly 100 μs before it disintegrates: $CO_2^- \rightarrow CO_2 + e^-$.[2]

1. G.R. Somayajulu, *Dissociation Energies of Diatomic Molecules*, J. Chem. Phys. 33 (1960) 1541.

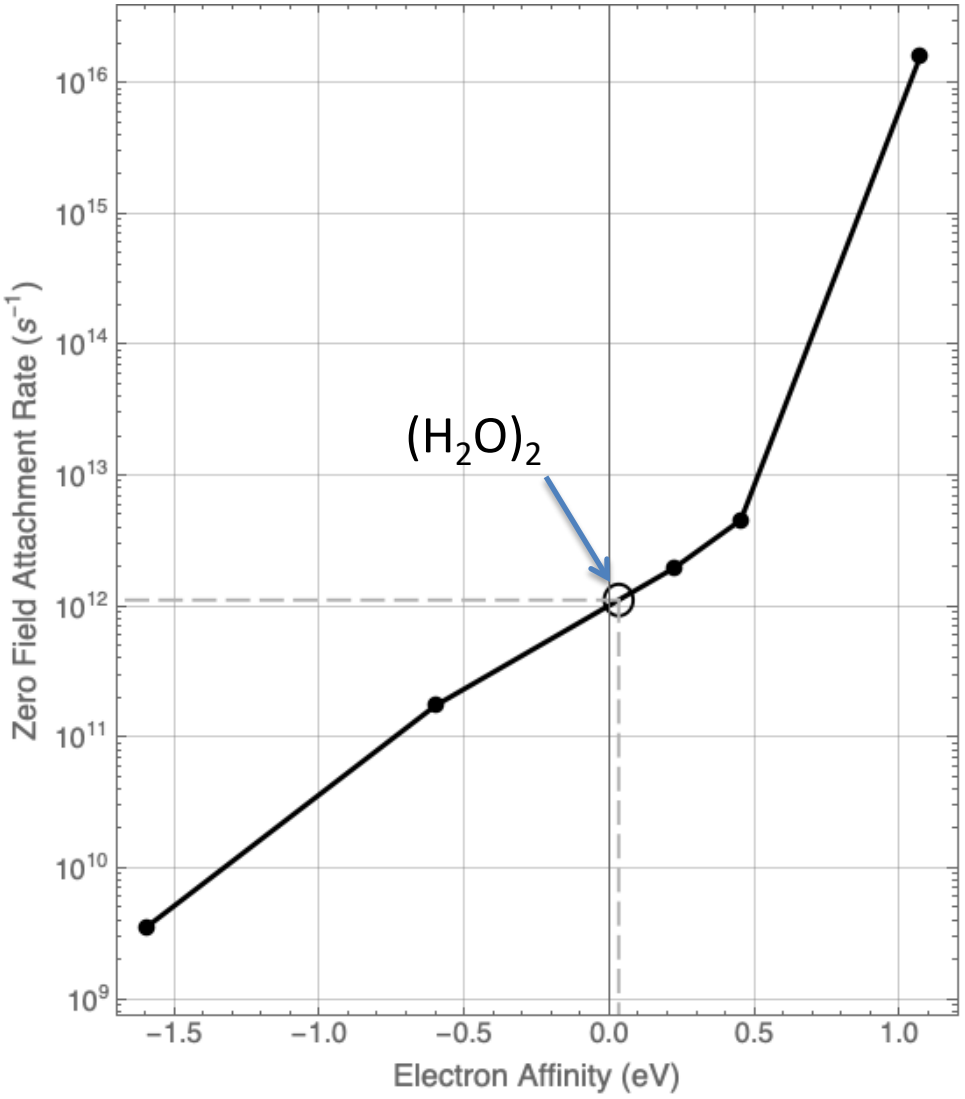
2. J.C. Rienstra-Kiracofe, et al., *Atomic and Molecular Electron Affinities: Photoelectron Experiments and Theoretical Computations*

Similar order to that for attachment rate:

$SF_6 > N_2O \sim O_2 > CO_2 \sim H_2O > N_2$

Observed Correlation between Electron Affinity and Electron Attachment Rate

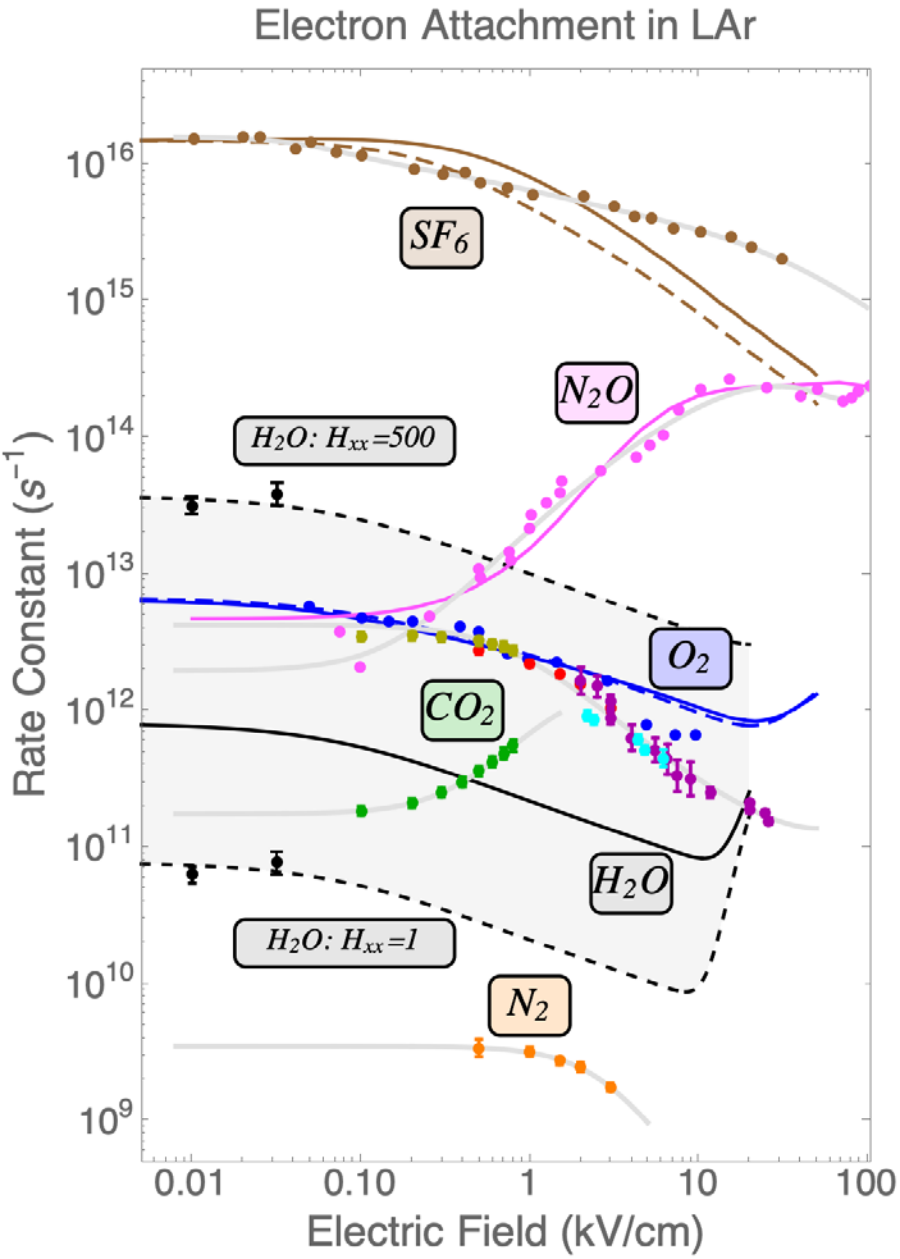
High electron affinity is associated with large direct attachment cross section.



Measured attachment rates (at zero field) and measured electron affinities (negative numbers are calculations). The attachment rate for $(H_2O)_2$ is found by interpolation to be 1.13 x 10^{12} s^{-1}.

Species	$k_{ATT}[0]$ (s^{-1})	EA (eV)
SF_6	1.61×10^{16}	1.1
O_2	4.60×10^{12}	0.45
N_2O	1.97×10^{12}	0.22
water	1.13×10^{12}	0.03
CO_2	1.77×10^{11}	−0.6
N_2	3.53×10^{9}	−1.6

Calculated Attachment Rates



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   a) The solid black line matches the low field attachment implied by the measured electron affinity (see slide 25)
   b) The two dashed black lines match the minimum and maximum values implied by our analysis of the Carls and the Andrews data, respectively.

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2. R. Andrews, et al., NIM A608 (2009) 251.

Some Estimates for Properties of H_2O in LAr

1. Henry's coefficient is between 0.004 and 0.04 (0.013 within a factor of 3).
2. The attachment rate constant is 10^{12} mole/s within a factor of 10.
3. The solubility is between 10 ppb and 300 ppb.
4. The adsorbed surface coverage is of the order of several monolayers at 100 ppb.

Needed to achieve “To Do” items

1. A purity monitor that operates at fields up to at least 1 kV/cm
2. A system with low leak rate to atmosphere ($<10^{-12}$ mole/s)
3. A way to introduce controllable, small amounts of impurity into the gas and the liquid (a controlled leak valve).
4. Maintain the LAr level (compensate for the loss by sampling) to the LAr level constant.
5. Add a mass flowmeter between the purifier and the condenser to measure the evaporation rate.
6. Increase the surface area of the LAr heater to avoid boiling.
7. A mechanism to move the sampling tube across the gas-liquid interface easily and quickly, without allowing air leaks.
8. A source of Ar saturated with water to control water leak rate.
9. Use purified GAr to purge the system, including gas analyzers, before the start of measurements.
10. A baffle that can be moved from below to above the gas recirculation inlet.
11. An RGA (mass spectrometer) to measure impurities other than O_2, N_2, and H_2O

We need to understand the response of the water concentration analyzer below 1ppb.

Response of H_2O Analyzer to Gas Dilution

Moisture concentration measured in the 20L system flowing GAr through either the purifier or the hot getter. The time dependence should be a simple exponential.